

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference C7755 (V)	FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, item 5 below.	
International application No. PCT/EP2004/013249	International filing date (day/month/year) 19/11/2004	(Earliest) Priority Date (day/month/year) 19/12/2003
Applicant UNILEVER N.V.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 6 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ The international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☐ **Certain claims were found unsearchable** (See Box II).

3. ☐ **Unity of invention is lacking** (see Box III).

4. With regard to the title,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

DETERGENT GRANULES AND PROCESS FOR THEIR MANUFACTURE

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the drawings,

- a. the figure of the **drawings** to be published with the abstract is Figure No. _____

☐ as suggested by the applicant.

☐ as selected by this Authority, because the applicant failed to suggest a figure.

☐ as selected by this Authority, because this figure better characterizes the invention.

- b. ☐ none of the figures is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP2004/013249

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D17/00 C11D3/50 C11D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 03/089019 A (PROCTER & GAMBLE) 30 October 2003 (2003-10-30) claims 1-11	1-15
A	WO 91/13143 A (MINNESOTA MINING & MFG ; PROCTER & GAMBLE (US)) 5 September 1991 (1991-09-05) claims 1-11	1-15
A	EP 0 397 245 A (PROCTER & GAMBLE) 14 November 1990 (1990-11-14) claims 1-14	1-15
A	US 5 188 753 A (SCHMIDT DIANE G ET AL) 23 February 1993 (1993-02-23) column 3, line 55 - column 4, line 15; claims 1-7	1-15
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

S document member of the same patent family

Date of the actual completion of the international search

8 April 2005

Date of mailing of the international search report

20/04/2005

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Form PCT/SA/210 (continuation of second sheet) (January 2004)

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CPY - KOBAYASHI

- TAKA-N

- TONA-N

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FS - CPI

IC - C08K9/10 ; C09D5/00 ; C09D7/12

MC - A08-M04 A12-B09 A12-W05 G02-A05

PA - (KOBAYASHI) KOBAYASHI KORYO KK

- (TAKA-N) TAKARA KOMUTEN KK

- (TONA-N) TONAN KAIHATSU BOEKI KK

PN - JP6329953 A 19941129 DW199507 C09D5/00 005pp

PR - JP19930142977 19930521

XA - C1995-022333

XIC - C08K-009/10 ; C09D-005/00 ; C09D-007/12

AB - J06329953 Perfume contained coating compsn. for wooden material comprises perfume contained micro-capsule having 5-15 microns capsule diameter and specific gravity of +0.35-0.05 higher than that of base coating (pref. clear lacquer at 40-100 times of micro-capsule wt.).

- Coating may involve 1) undercoating with mixture of new coating compsn. and sealant and 2) over coating with new coating compsn.

- USE/ADVANTAGE - Coating compsn. is coated on wooden material, and provides long lasting odour on wooden material, and new coating method provide strong adhesive strength against wooden surface.

- Example coating compsn. is 1) 1 pts.wt. melamine resin microcapsules contg. Hinoki cypress oil, having 1.2 specific gravity, having dia. of around 10 microns, and obtd. by coacervation-phase sepn. method and 2) 100 pts.wt. clear lacquer having 0.89-0.98 specific gravity.(Dwg.0/0)

IW - PERFUME CONTAIN COATING COMPOSITION WOOD MATERIAL PERFUME CONTAIN MICROCAPSULE SPECIFIC CAPSULE DIAMETER SPECIFIC GRAVITY OPTION CLEAR LACQUER

IKW - PERFUME CONTAIN COATING COMPOSITION WOOD MATERIAL PERFUME CONTAIN MICROCAPSULE SPECIFIC CAPSULE DIAMETER SPECIFIC GRAVITY OPTION CLEAR LACQUER

NC - 001

OPD - 1993-05-21

ORD - 1994-11-29

PAW - (KOBAYASHI) KOBAYASHI KORYO KK

- (TAKA-N) TAKARA KOMUTEN KK

- (TONA-N) TONAN KAIHATSU BOEKI KK

TI - Perfume contained coating compsn. for wooden material - with perfume contained microcapsules having specific capsule dia. and specific gravity, and opt. clear lacquer

A01 - [001] 017 ; R00859 G1809 G1649 D01 D23 D22 D31 D45 D50 D83 F19 F10 F07 ; H0011-R ; P0259-R P0226 D01 ; H0293 ;

- [002] 017 ; ND04 ; ND01 ; Q9999 Q7523 ; Q9999 Q7114-R ; K9609 K9483 ; K9676-R ; B9999 B5301 B5298 B5276 ;

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German patent DD 295 761 A5

Berlin-Kosmetik GmbH

Process for the preparation of amino resin microcapsule dispersions for cosmetic compositions

Melamine-formaldehyde resins; melamine-urea-formaldehyde resins; microcapsules; formaldehyde; gelatine; cosmetics; perfume oil

The invention relates to a process for the preparation of amino resin microcapsule dispersions containing not more than 0.2 wt-% of free formaldehyde. It is used in the manufacture of microcapsule dispersions used in contact with human skin, for example in the cosmetic or medical field. Encapsulated perfume oil is especially useful for use in water-in-oil and oil-in-water emulsions such as creams, lotions and masks.

Claims

1. A process for the preparation of amino resin microcapsule dispersions for cosmetic compositions based on partially methanol-etherified, cationically modified water-soluble melamine-formaldehyde resins or melamine-urea-formaldehyde resins in which from 25 to 75% of the hydroxymethyl groups are etherified, characterised in that from 1 to 200 g of gelatine per 100 g of amino resin used for encapsulation are added in an aqueous solution heated to 30-70 °C to the amino resin microcapsule dispersions before, during or after capsule formation.
2. A process according to claim 1, characterised in that gelatine is added in amounts of from 25 to 50 g per 100 g of the encapsulating amino resin.
3. A process according to claim 1 characterised in that the aqueous gelatine solution contains 10 g of gelatine per 100 ml of water.
4. A process according to claims 1 to 3, characterised in that the temperature of the gelatine solution is between 40 and 65 °C.

5. A process according to claims 1 to 4, characterised in that the gelatine solution is added to the dispersion over a period of 1-60 minutes.

6. A process according to claim 1, characterised in that a perfume oil is encapsulated.

7. A process according to claims 1 and 6, characterised in that the perfume oil is incorporated into water/oil or oil/water emulsions.

8. A process according to claims 1 and 6, characterised in that the encapsulated perfume oil is incorporated into powder mixtures.

9. A process according to claim 1 and 6, characterised in that the encapsulated perfume oil is incorporated into surfactants for shampoos, shower products or bath foams.

Field of the invention

The invention relates to a process for the preparation of amino resin microcapsules that contain water-insoluble or sparingly water-soluble substances as the core material and can be used in cosmetic compositions.

Features of the prior art

The use of microencapsulated odorous materials in cosmetics is known. For example, DE AS 23 117 12 discloses the preparation of microcapsules by the interfacial polyaddition of isocyanate prepolymers and diamines. Substances that are encapsulated by this method include leather perfume and lavender perfume. The encapsulation of perfumes is also mentioned in

DD 141 113, and diisocyanates and diamines are likewise used in this process to form the capsule walls.

Microcapsules obtained with the use of isocyanates are not suitable for use in cosmetic preparations because the highly-toxic isocyanates are used in direct contact with the active

ingredients that are to be encapsulated and are present inside the capsules, and there is the risk of the isocyanates not reacting completely during the formation of the capsule walls.

Isocyanates released with the perfumes when the microcapsules are used can cause serious injury to the skin.

Without using toxic isocyanates, microcapsules can be prepared from amino resins, in other words the reaction products of urea, melamine or other suitable compounds, with formaldehyde. These processes have the advantage that only one component is needed to form the capsule walls. Because amino resins are used in a great many processes for the encapsulation of water-insoluble dye precursor products for the manufacture of colour-react papers, some disclosures also mention perfumes among the substances that are encapsulated. Examples of such disclosures are US P 3,516,846, 3,516,941, EP 142 242, DD 241 566, US P 2826860, US P 4,087,376, EP 321 750.

Perfume-containing microcapsules manufactured according to US P 3,516,846, are used to coat writing paper.

The direct use of cosmetic active ingredients microencapsulated with amino resins is described in EP 254 447. Here, solutions of bactericides in long-chain alcohol benzoates are thickened with butadiene-styrene block copolymers and encapsulated with amino resins according to US P 2,516,941. By thickening the liquid core material, the capsules can be enlarged by comparison with the teaching of US P 3,516,041 to a size of 60-120 μm , which results in a mild abrasive action on the skin as well as releasing the perfume during use.

When an attempt was made to produce microencapsulated perfumes and bactericides in accordance with the teaching of EP 254 447, it was found that because of their size, the resulting capsules were for the most part destroyed when subjected to shearing during their incorporation into for example deodorant sticks, creams and other products, so that the undesired [*sic*] long-lasting action was not obtained.

Another major disadvantage that is inherent in all amino resins, even etherified precondensates

(EP 152 083, DD 241 536) hitherto used to encapsulate perfumes, is that the microcapsule dispersions obtained by this method still contain at least 0.30 wt-% of free formaldehyde. It has long been known that formaldehyde can cause allergies on contact with the skin, so that microcapsule dispersions obtained by the known methods cannot be used for cosmetic compositions. Numerous proposals have already been made for reducing the content of free formaldehyde in microcapsule dispersions, especially for use for coating paper, and they are discussed in a review article (Acta Polymerica, 40 [1989], 243). All of the additives mentioned therein except for urea are not suitable for cosmetic compositions; however, the addition of urea has an adverse effect on capsule properties (Acta Polymerica, 40 [1980] 683), so that to date no additive is known that combines the irreversible reduction of the free formaldehyde content of amino resin microcapsule dispersions with dermatological innocuousness.

Object of the invention

The object of the invention is to provide a technically simple and economically advantageous process for the preparation of amino resin microcapsule dispersions whose free formaldehyde concentration is so low that they can be safely used in the manufacture of cosmetic preparations.

Description of the invention

The aim of the invention is to use selected additives to reduce the concentration of free formaldehyde in amino resin microcapsule dispersions, particularly for their use in cosmetics, to a maximum of 0.2 wt-%.

In the invention, this aim is achieved by preparing the microcapsule dispersions in the presence of dissolved gelatine.

This solution was particularly surprising because it was found in a series of experiments with proteins and protein-containing substances such as collagen, whey powder, yeast, yeast extracts, gelatine and so forth, that gelatine was the only compound that reacted with free

formaldehyde under the reaction conditions of microencapsulation and so helped reduce the free formaldehyde content.

By gelatine there is understood herein products that are obtained from hides or bones by acid or alkaline treatment followed by further processing and described in "Encyclopedia of Polymer Sci. and Engineering" (Wiley and Sons, Vol. 7, page 488 [1987]).

The amount of gelatine added is 1-200 g and preferably 25-50 g, calculated on the amount of amino resin used for microencapsulation. The gelatine is usefully added in the form of a hot aqueous solution, for example having a concentration of 10 wt-%. As wall-forming materials there are used per se known aqueous amino resin solutions based on partially methanol-etherified water-soluble melamine-formaldehyde resins or melamine-urea-formaldehyde resins, in which 25-75% of the hydroxymethyl groups are etherified. Cationic modifiers, preferably alkanolamines such as mono, di or triethanolamine, can be added to the resins. Capsule formation is obtained by mixing an aqueous amino resin solution having an amino resin concentration of 0.5-20 g per 100 ml of water with the substance that is to be encapsulated, mixing being carried out under high shear in the case of liquids. The resulting dispersion is brought to a temperature between 30 and 70 °C and preferably 40 and 85 °C. Before, during or after the dispersion step or reaching the selected reaction temperature, the pH is adjusted to a value between 2.5 and 6. If a liquid substance is to be encapsulated, the dispersion is stirred for 1-240 minutes and preferably 1-60 minutes, with high shear, at a temperature between 30 and 70 °C, and in the case of solid substances, stirring is carried out under low shear in the same temperature range.

The capsule dispersion is then stirred under low shear for from 15 minutes to 8 days, preferably for 2 to 10 hours at a temperature between 30 and 70 °C and/or is held without stirring for 3 to 7 days in the same temperature range. The gelatine can be added before, during or after capsule formation.

The content of free formaldehyde in the microcapsule dispersions prepared in accordance with the invention is less than 0.2 wt-%. Free formaldehyde is determined by polarography (see R. Nastke, K. Dietrich and W. Teige, Acta Polymerica 31 [1980], 329).

Preferably, the substances that are encapsulated are substances that are used as components of cosmetic preparations. These are for example perfume oils, odorous materials, and flavours; these materials are not usually pure substances but mixtures of active components. The only criterion is that their water-solubility should be low. It is also possible to use dissolved substances, for example bactericides, as the core material; in these cases, dermally-tolerated oils such as castor oil, paraffin oil, fatty acid esters and the like are preferably used as solvents.

The substances used must have boiling points lying above the reaction temperature during capsule manufacture.

Solids can be milled to the required particle size beforehand and then dispersed in the capsulation medium.

The reaction pH is adjusted with organic or mineral acids, with organic acids, for example citric acid, being preferred for cosmetic preparations.

Perfume oil can be especially advantageously encapsulated by the process of the invention. It is a particular advantage that the fragrance is only developed when it is on the skin.

This encapsulated perfume oil can be used in a multiplicity of cosmetic preparations. For example, its use in water/oil emulsions such as creams or lotions, or in oil/water emulsions, such as masks or day creams, is advantageous. Encapsulated perfume oil has also been successfully incorporated into powder mixtures, for example deodorant powders.

Another application is in surfactant mixtures of the kind used for shampoos, shower products and bath foams.

In all of these cases, it is necessary to incorporate the encapsulated perfume oil dispersion with particular care, without the use of high shear forces.

The extremely low formaldehyde content makes the use of encapsulated material acceptable in cosmetic preparations.

Examples

The process of the invention and the use of the encapsulated material are described in greater detail below, with reference to examples.

The following aqueous solutions of partially methanol-etherified, cationically-modified amino resins obtained in a manner known per se were used as the wall-forming materials:

Resin type I

Reaction product of 1 mole of melamine and 6 moles of formaldehyde, cationically modified with triethanolamine after etherification with methanol, and containing 1.23 moles of free methylol groups. The solids content was adjusted to 50 wt-%.

Resin type II

Reaction product of 1 mole of melamine and 0.1 mole of urea with 5.6 moles formaldehyde, cationically modified with triethanolamine after etherification with methanol and containing 1.53 moles of free methylol groups. The solids content was adjusted to 50 wt-%.

Example 1

A mixture of 60 ml of water, 3.0 g of aqueous type 1 resin solution and 30 g of perfume oil in a mixture of saturated fatty acid esters was heated with a dispersant to 60 °C, with stirring. The mixture was adjusted to pH 4 with the addition of 2.0 g 2N citric acid and mixed under high shear for 6 minutes. Thereafter, the mixture was stirred for 4 hours at 60 °C. After placing on slides and after the water had evaporated off, tenacious capsules having a mean diameter of 12 µm were obtained.

The free formaldehyde content of the capsule dispersion was 0.30 wt-%.

The encapsulated perfume oil was used in a water-in-oil emulsion for a lotion or a cream.

Formulation: Cream	Lotion	
74.2%	85.3%	water
2.5%	3.5%	silicone oil
3.5%	2.5%	paraffin oil
10.5%	6.4%	emulsifier
3.8%	2.8%	Vaseline
5.5%	3.0%	lanolin
0.2%	0.2%	perfume oil dispersion
0.3%	0.3%	preservative

The encapsulated perfume oil dispersion was added to the emulsion at a temperature of 28-30 °C with very slow stirring. Care must be taken not to destroy the capsules during stirring. The free unencapsulated perfume oil (1-5 wt-%) in the capsule dispersion confers an immediate fragrancing effect on the emulsion. The encapsulated perfume oil in the dispersion is not released until it is applied to the skin. Repeated rubbing over the skin surface releases the deposited fragrance and the pleasant fragrance note lasts for up to 12 hours.

This encapsulating method can also be used to save from 60 to 80 wt-% of the usual amount that would otherwise be used.

Example 2

Example 1 was repeated with the difference that the quantity of resin was reduced to 2.5 g. The corresponding amount of 2N citric acid was 1.66g. The free formaldehyde content in the capsule dispersion was 0.2 wt-%. The encapsulated perfume oil was incorporated into a mask as an oil-in-water emulsion.

Formulation:

75.5% water
0.3% Vaseline
3.5% lanolin
12.5% emulsifier
0.2% preservative
2.2% propylene glycol
1.0% sesame oil
1.0% vitamin E
1.0% vitamin A
0.1% encapsulated perfume oil dispersion.

The method of incorporation was the same as in Example 1.

Example 3

Examples 1 and 2 were repeated and modified by emulsifying the 30 g of perfume oil solution in a mixture of 50 ml of water and 10 g of a 10% aqueous solution of gelatine. Different amounts of amino resin were used in combination with gelatine and 2N citric acid. Advantageous quantities were 3 g of resin I and 2.0 ml of 2N citric acid. The free formaldehyde content in the capsule dispersion was 0.15 wt-%.

The perfume oil encapsulated in accordance with this Example was used in a day cream which was a water-in-oil emulsion.

Formulation:

- 7.5% coco isooctyl ester
- 2.5% propylene glycol
- 0.3% preservative
- 3.5% colour
- 0.2% encapsulated perfume oil dispersion
- 3.5% emulsifier
- 82.5% water

The colour was added to the water phase and thoroughly dispersed. The method of incorporation was the same as that in Example 1.

Example 4

76 ml of water, 15 g of 10% gelatine solution, 45 g of perfume oil and 4.5 g of resin I were stirred under high shear, heated to 60 °C and 3 ml of 2N citric acid were added when this temperature had been reached. The mixture was stirred under high shear for a further 5 minutes, and was then kept at 60 °C under low shear for 4 hours.

Tenacious microcapsules with a mean diameter of 15.8 µm were obtained. The free formaldehyde content in the capsule dispersion was 0.17 wt-%. This material was suitable for the preparation of a perfume emulsion.

Formulation: 64.3 - 75.6% water
12.3% emulsifiers
2.0% silicone oil
4.2% lanolin
5.5 - 15.0% encapsulated perfume oil dispersion
0.2% preservative

The preparation was carried out by mixing the components and then incorporating the encapsulated perfume oil dispersion.

Example 5

To 15 g of a 10% aqueous solution of gelatine there were added one after the other, in 90 ml of water at 40 °C and under high shear, 45 g of orange oil, 4.5 g of type II resin, and 3 ml of 2N citric acid. After stirring for 5 minutes at 40 °C under high shear, the mixture was stirred at 40 °C for a further 4 hours.

The resulting microcapsule dispersion contained 0.12 wt-% of free formaldehyde.

The encapsulated perfume oil dispersion thereby obtained was incorporated into a face powder.

Formulation: 84.0% talcum
10.0% kaolin
2.4% magnesium stearate
1.5% binder
2.0% colour pigments
0.1% encapsulated perfume oil dispersion.

The encapsulated perfume oil dispersion was carefully mixed into the finished powder mixture at room temperature and then applied.

Example 6

60 ml of water and 10 g of a 10% solution of gelatine were thoroughly mixed, and to this mixture there were added one after the other 3 g of resin I and 30 g of perfume oil. The mixture was heated to 60 °C with stirring under high shear and 2 ml of 2N citric acid solution were added. After stirring for 10 minutes under vigorous shear, stirring was continued for 5 hours at 65 °C. The resulting capsule dispersion had a free formaldehyde content of

0.12 wt-%. This time, the perfume oil dispersion was incorporated into an eye-shadow powder.

Formulation:

- 70.0% talcum
- 10.0% kaolin
- 4.0% stearates
- 2.0% binders
- 3.9% colour pigments
- 10.0% lustre pigments
- 0.1% encapsulated perfume oil dispersion

Processing was the same as in Example 5.

Example 7

60 ml of water, 30 g of perfume oil and 3.0 g of resin were stirred under high shear, heated to 60 °C and when this temperature had been reached, 2.0 ml of 2N citric acid were added. Stirring was continued under high shear for a further 5 minutes, then under low shear for 1 hour at 60 °C.

To the microcapsule dispersion there were added 15 ml of a 10% gelatine solution and the mixture was held for a further 3 hours at 60 °C. The capsule dispersion had a free formaldehyde content of 0.1 wt-%.

The encapsulated perfume oil was used in surfactant mixtures such as shampoos, shower products or bath foams.

Formulation:

- 40.5% water
- 22.0% fatty alcohol sulphate
- 25.2% sulphobetaines
- 0.3% preservative
- 1.5% wheat germ oil
- 0.5% encapsulated perfume oil dispersion

The perfume oil dispersion was added to and dispersed in the finished surfactant mixture with slow and gentle stirring at room temperature.



(12) Ausschließungspatent

(11) DD 295 761 A5

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(74)	Berlin-Kosmetik GmbH, Anklamer Straße 38, O - 1040 Berlin, DE				
(54)	Verfahren zur Herstellung von Aminoharz-Mikrokapseldispersionen für kosmetische Präparate				

(55) Melamin-Formaldehyd-Harze; Melamin-Harnstoff-Formaldehyd-Harze; Mikrokapseln; Formaldehyd; Gelatine; Kosmetik; Parfümöl

(57) Die Erfindung betrifft ein Verfahren zur Herstellung von Aminoharz-Mikrokapseldispersionen mit Gehalten an freiem Formaldehyd von maximal 0,2 Masseanteilen in %. Sie findet Anwendung bei der Herstellung von Mikrokapseldispersionen, die in Kontakt mit menschlicher Haut verwendet werden, beispielsweise auf dem Gebiet der Kosmetik oder der Medizin. Besonders geeignet ist der Einsatz von verkapseltem Parfümöl bei Wasser in Öl und Öl in Wasser-Emulsionen, wie Cremes, Lotionen oder Masken.

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Patentansprüche:

1. Verfahren zur Herstellung von Aminoharz-Mikrokapseldispersionen für kosmetische Präparate auf der Basis partiell methanolveretherter, kationisch modifizierter, wasserlöslicher Melamin-Formaldehyd-Harze oder Melamin-Harnstoff-Formaldehyd-Harze, in denen 25 bis 75% der Hydroxymethylgruppen verethert sind, gekennzeichnet dadurch, daß der Aminoharz-Mikrokapseldispersion vor, während oder nach der Kapselbildung 1 bis 200 g Gelatine pro 100 g zum Verkapseln verwendeten Menge Aminoharz in einer 30 bis 70°C warmen wäßrigen Lösung zugesetzt werden.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Gelatine in Mengen von 25 bis 50 g pro 100 g zu verkapselnder Aminoharzmenge zugesetzt wird.
3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die wäßrige Lösung der Gelatine 10 g Gelatine pro 100 ml Wasser enthält.
4. Verfahren nach Anspruch 1 bis 3, dadurch gekennzeichnet, daß die Temperatur der Gelatinelösung zwischen 40 und 65°C liegt.
5. Verfahren nach Anspruch 1 bis 4, dadurch gekennzeichnet, daß die Gelatinelösung über einen Zeitraum von 1 bis 60 min der Dispersion zugesetzt wird.
6. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß ein Parfümöhl verkapselt wird.
7. Verfahren nach Anspruch 1 und 6, dadurch gekennzeichnet, daß das Parfümöhl in Wasser/Öl- oder Öl/Wasser-Emulsionen eingearbeitet wird.
8. Verfahren nach Anspruch 1 und 6, dadurch gekennzeichnet, daß das verkapselte Parfümöhl in Pudermischungen eingearbeitet wird.
9. Verfahren nach Anspruch 1 und 6, dadurch gekennzeichnet, daß das verkapselte Parfümöhl in Tensiden für Shampoo, Duschbäder oder Schaumbäder eingearbeitet wird.

Anwendungsgebiet der Erfindung

Die Erfindung betrifft ein Verfahren zur Herstellung von Aminoharz-Mikrokapseln, die als Kernmaterial wasserunlösliche oder schwer in Wasser lösliche Substanzen enthalten und in kosmetischen Präparaten eingesetzt werden können.

Charakteristik des bekannten Standes der Technik

Die Verwendung mikroverkapselter Geruchsstoffe in der Kosmetik ist bekannt. Beispielsweise wird in der DE-AS 2311712 die Herstellung von Mikrokapseln durch Grenzflächenpolyaddition von Isocyanat-Präpolymeren und Diaminen beschrieben. Unter den nach diesem Verfahren zu verkapselnden Substanzen werden auch Lederparfüm und Lavendelparfüm genannt. Die Verkapselung von Parfümen wird auch in DD-PS 141 113 erwähnt, auch bei diesem Verfahren werden Diisocyanate und Diamine zur Bildung der Kapselwände eingesetzt.

Unter Verwendung von Isocyanaten hergestellte Mikrokapseln sind für die Verwendung in kosmetischen Zubereitungen nicht geeignet, da die hochgiftigen Isocyanate in direktem Kontakt mit den zu verkapselnden Wirkstoffen eingesetzt werden, sich im Inneren der Kapseln befinden und die Gefahr besteht, daß die Isocyanate bei der Bildung der Kapselwände nicht vollständig umgesetzt werden. Die beim Gebrauch der Mikrokapseln mit den Duftstoffen freigesetzten Isocyanate können schwere Schäden auf der Haut verursachen.

Ohne Verwendung der giftigen Isocyanate können Mikrokapseln aus Aminoharzen d.h. Reaktionsprodukten von Harnstoff, Melamin oder anderen geeigneten Verbindungen mit Formaldehyd hergestellt werden. Diese Verfahren haben zunächst den Vorteil, daß nur eine Komponente zur Bildung der Kapselwände benötigt wird. Da Aminoharze in einer Vielzahl von Verfahren für die Verkapselung wasserunlöslicher Farbstoffvorprodukte für die Herstellung von Reaktionsdurchschreibepapieren verwendet werden, werden in einigen dieser Offenbarungen auch Duftstoffe unter den zu verkapselnden Stoffen genannt. Beispiele für solche Offenbarungen sind US-PS 3516846, 3516941, EP-PS 142242, DD-PS 241556, DE-PS 2926860, US-PS 4087376, EP-PS 321750.

Nach den US-PS 3516846 und 3516941 hergestellte parfümhaltige Mikrokapseln werden zur Beschichtung von Schreibpapier verwendet.

Die direkte Verwendung von mit Aminoharzen mikroverkapselten kosmetischen Wirkstoffen ist in EP-PS 254447 beschrieben. Dabei werden Lösungen von Bakteriziden in Benzoaten langkettiger Alkohole mit Butadien-Styren-Blockcopolymeren verdickt und mit Aminoharzen entsprechend US-PS 3516941 verkapselt. Durch die Verdickung des flüssigen Kernmaterials wird gegenüber der Lehre aus US-PS 3516941 eine Vergrößerung der Kapseln auf 50 bis 2000 µm erreicht, wodurch neben der Freisetzung des Duftstoffs beim Gebrauch noch eine milde abrasive Wirkung auf der Haut erreicht wird.

Beim Versuch, entsprechend der Lehre von EP-PS 254447 mikroverkapselte Duftstoffe und Bakterizide herzustellen, hat sich gezeigt, daß die so erhaltenen Kapseln jedoch infolge ihrer Größe unter der Scherwirkung bei der Konfektionierung zu beispielsweise Deostiften, Cremes und anderen Produkten zum großen Teil zerstört werden, so daß die unerwünschte Dauerwirkung nicht erreicht wird.

Daneben zeigte sich noch ein weiterer schwerwiegender Nachteil, der auch allen bisher für die Verkapselung von Duftstoffen eingesetzten Aminoharzen, auch veretherter Vorkondensaten, (EP-PS 152083, DD-PS 241 536) eigen ist: Die nach diesen Verfahren hergestellten Mikrokapsel-Dispersionen enthalten noch mindestens 0,30 Masseanteile in % freiem Formaldehyd. Es ist auch lange bekannt, daß Formaldehyd bei Kontakt mit der Haut zu Allergien führen kann, so daß die nach den bekannten Verfahren hergestellten Mikrokapsel-Dispersionen nicht für kosmetische Zubereitungen verwendet werden können. Für die Verringerung des Gehaltes an freiem Formaldehyd in Mikrokapsel-Dispersionen, besonders für die Verwendung zur Papierbeschichtung, gibt es bereits zahlreiche Vorschläge, die in einer Übersicht zusammengefaßt sind (Acta Polymerica, 40 [1989], 243). Alle dort angeführten Zusatzstoffe bis auf Harnstoff eignen sich nicht für kosmetische Präparate, der Zusatz von Harnstoff verschlechtert jedoch die Kapsel Eigenschaften (Acta Polymerica 40 [1980], 683), so daß bisher kein Zusatzstoff bekannt war, der die irreversible Herabsetzung des Gehaltes an freiem Formaldehyd in Aminoharz-Mikrokapseldispersionen mit dermatologischer Unbedenklichkeit verbindet.

Ziel der Erfindung

Die Erfindung hat das Ziel, ein technisch einfaches und ökonomisch vorteilhaftes Verfahren zur Herstellung von Aminoharz-Mikrokapseldispersionen mit einer so niedrigen Konzentration an freiem Formaldehyd zu schaffen, daß diese Kapseldispersionen unbedenklich für die Herstellung kosmetischer Präparate verwendet werden können.

Darlegung des Wesens der Erfindung

Der Erfindung liegt die Aufgabe zugrunde, die Konzentration an freiem Formaldehyd in Aminoharz-Mikrokapseldispersionen, speziell für deren Verwendung in der Kosmetik auf maximal 0,2 Masseanteile in % durch ausgewählte Zusatzstoffe zu erniedrigen.

Erfindungsgemäß wurde die Aufgabe dadurch gelöst, daß die Herstellung der Mikrokapsel-Dispersion in Gegenwart von gelöster Gelatine erfolgt.

Die Lösung war deshalb besonders überraschend, da aus einer Reihe von Versuchen mit Proteinen bzw. proteinhaltigen Substanzen wie Kollagen, Molkepulver, Hefe, Hefeextrakten, Gelatine u. a. hervorging, daß als einzige Verbindung Gelatine unter den Reaktionsbedingungen der Mikroverkapselung mit dem freien Formaldehyd reagiert und so zu einer Absenkung des Gehaltes an freiem Formaldehyd beiträgt.

Unter Gelatine werden in dieser Erfindung Produkte verstanden, die aus Häuten oder Knochen durch Säure- oder Alkalibehandlung mit anschließender Aufbereitung gewonnen werden und in „Encyclopedia of Polymer Sci. and Engineering“ (Wiley u. Sons, Bd. 7, S. 488 [1987]) beschrieben sind.

Die Menge zugesetzter Gelatine beträgt 1 bis 200 g, vorzugsweise 25 bis 50 g, bezogen auf die zum Mikroverkapseln verwendete Menge an Aminoharz, der Zusatz an Gelatine erfolgt zweckmäßigerweise aus warmer wäßriger Lösung, beispielsweise mit einer Konzentration von 10 Masseanteilen in %. Als wandbildende Materialien werden an sich bekannte wäßrige Aminoharzlösungen auf Basis partiell methanolveretherter wasserlöslicher Melamin-Formaldehyd-Harze oder Melamin-Harnstoff-Formaldehyd-Harze eingesetzt, in denen 25 bis 75% der Hydroxymethylgruppen verethert sind. Die Harze können mit kationischen Modifikatoren vorzugsweise Alkanolaminen wie Mono-Di- oder Triethanolamin, versetzt werden. Die Kapselbildung erfolgt so, daß eine wäßrige Aminoharzlösung mit einer Konzentration an Aminoharz von 0,5 bis 20 g pro 100 ml Wasser mit der zu verkapselnden Substanz vermischt wird, wobei bei Flüssigkeiten die Vermischung unter hoher Scherung erfolgt. Die entstandene Dispersion wird auf eine Temperatur zwischen 30 und 70°C, vorzugsweise 40 bis 65°C gebracht. Vor, während oder nach dem Dispergiervorgang bzw. dem Erreichen der gewählten Reaktionstemperatur wird der pH-Wert auf einen Wert zwischen 2,5 bis 6 eingestellt. Die Dispersion wird bei Verwendung flüssiger zu verkapselnder Substanz 1 bis 240 min, vorzugsweise 1 bis 60 min, unter hoher Scherung bei einer Temperatur zwischen 30 und 70°C gerührt, bei festen Substanzen erfolgt das Rühren unter niedrigen Scherungen im gleichen Temperaturintervall.

Die Kapseldispersion wird danach bei einer Temperatur zwischen 30 und 70°C 15 min bis 8 Tage, vorzugsweise 2 bis 10 Stunden unter niedriger Scherung gerührt und/oder für 3 bis 7 Tage ohne Rühren in dem genannten Temperaturbereich aufbewahrt. Der Zusatz der Gelatine kann vor, während oder nach der Kapselbildung erfolgen.

Der Gehalt an freiem Formaldehyd in den erfindungsgemäß hergestellten Mikrokapseldispersionen beträgt unter 0,2 Masseanteilen in %. Die Bestimmung des freien Formaldehyds erfolgte durch Polarographie (vgl. R. Nastke, K. Dietrich u. W. Teige, Acta Polymerica 31 [1980], 329).

Als zu verkapselnde Substanzen werden vorzugsweise solche eingesetzt, die als Komponenten in Zubereitungen für die Kosmetik verwendet werden. Das sind beispielsweise Parfümöle, Geruchsstoffe, Geschmacksstoffe, wobei die einzelnen Stoffe meist keine reinen Komponenten, sondern Wirkstoffgemische sind. Einziges Kriterium ist deren geringe Wasserlöslichkeit. Es ist weiterhin möglich, gelöste Stoffe, z. B. Bakterizide als Kernmaterial einzusetzen, als Lösungsmittel werden in diesen Fällen vorzugsweise hautverträgliche Öle, wie Rizinusöl, Paraffinöl, Fettsäureester u. a. eingesetzt.

Die eingesetzten Substanzen müssen eine Siedetemperatur aufweisen, die oberhalb der Reaktionstemperatur bei der Kapselherstellung liegt.

Feststoffe können vorher auf die gewünschte Korngröße aufgemahlen werden und dann im Kapselungsmedium dispergiert werden.

Die Einstellung des Reaktions-pH-Wertes erfolgt mit organischen oder anorganischen Säuren, wobei für Kosmetikpräparate organische Säuren, z. B. Zitronensäure, bevorzugt sein sollten.

Als besonders günstig kann nach dem erfindungsgemäßen Verfahren Parfümöl verkapselt werden. Es ist besonders vorteilhaft, daß sich auf der Haut erst der Duft entfaltet.

Dieses verkapselte Parfümöl ist in einer Vielzahl von kosmetischen Präparaten anwendbar. So ist der Einsatz in Wasser/Öl-Emulsionen, wie in Cremes oder Lotionen bzw. in Öl/Wasser-Emulsionen, wie bei Masken oder Tagescreme vorteilhaft. Erfolgreich wurde das verkapselte Parfümöl auch bei Pudermischungen, z.B. Deopudern eingearbeitet. Ein weiteres Anwendungsgebiet ist der Einsatz bei Mischungen von Tensiden, wie sie für Shampoo, Dusch- und Schaumbäder eingesetzt werden. In allen Fällen ist es erforderlich, die verkapselte Parfümöl-Dispersion besonders vorsichtig, ohne Anwendung hoher Scherkräfte einzuarbeiten. Durch den äußerst niedrigen Gehalt an Formaldehyd wird die Anwendung von verkapseltem Material auch in kosmetischen Präparaten erst vertretbar.

Ausführungsbeispiele

Das erfindungsgemäße Verfahren und die Anwendung des verkapselten Materials wird nachfolgend an den Ausführungsbeispielen näher erläutert.

Als wandbildende Materialien wurden die nachstehenden, wäßrigen Lösungen von in an sich bekannter Weise hergestellten partiell methanolveretherten, kationisch modifizierten Aminoharzen eingesetzt:

Harztyp I:

Reaktionsprodukt aus 1 Mol Melamin mit 6 Mol Formaldehyd, das nach der Veretherung mit Methanol durch Triethanolamin kationisch modifiziert wurde und 1,23 Mol freie Methylolgruppen besaß. Der Feststoffgehalt wurde auf 50 Masseanteile in % eingestellt.

Harztyp II:

Reaktionsprodukt aus 1 Mol Melamin und 0,1 Mol Harnstoff mit 5,6 Mol Formaldehyd, das nach der Veretherung mit Methanol durch Triethanolamin kationisch modifiziert wurde und 1,58 Mol freie Methylolgruppen besaß. Der Feststoffgehalt wurde auf 50 Masseanteile in % eingestellt.

Beispiel 1

Eine Mischung aus 60 ml Wasser, 3,0 g wäßriger Harzlösung vom Typ I und 30 g Parfümöl in einem Gemisch von Estern gesättigter Fettsäuren wird unter Rühren mit einem Dispergator auf 60°C erwärmt. Die Mischung wird durch Zusatz von 2,0 g 2 n Zitronensäure auf pH 4 eingestellt und 6 min unter hoher Scherung durchmischt. Danach wird die Mischung 4 Stunden bei 60°C gerührt. Nach Auftragen auf Objektträger und Verdunsten des Wassers werden trockenfeste Kapseln mit einem mittleren Durchmesser von 12 µm erhalten.

Der Gehalt an freiem Formaldehyd in der Kapseldispersion beträgt 0,30 Masseanteile in %.

Das so verkapselte Parfümöl wird in einer Wasser-in-Öl-Emulsion, die als Lotion oder Creme angewendet wird, eingesetzt.

Rezeptur:	Creme	Lotion	
	74,2%	85,3%	Wasser
	2,5%	3,5%	Silikonöl
	3,5%	2,5%	Paraffinöl
	10,5%	6,4%	Emulgator
	3,8%	2,8%	Vaseline
	5,5%	3,0%	Wollfett
	0,2%	0,2%	Parfümöl-Dispersion
	0,3%	0,3%	Konservierungsmittel

Die verkapselte Parfümöl-Dispersion wird bei einer Temperatur von 28 bis 30°C unter sehr langsamem Rühren der Emulsion zugesetzt. Es muß darauf geachtet werden, daß beim Einrühren die Kapseln nicht zerstört werden. Das in der Kapseldispersion freie unverkapselte Parfümöl (1 bis 5 Masseanteile in %) gibt der Emulsion die Sofortwirkung an Duft. Das verkapselte Parfümöl in der Dispersion wird erst während des Auftragens auf der Haut freigesetzt. Durch wiederholtes Streichen über die Hautoberfläche wird der deponierte Duft frei und eine angenehme Duftnote behält ihre Wirkung bis zu 12 Stunden. Es ist weiterhin möglich, durch das angegebene Verkapselungsverfahren 60 bis 80 Masseanteile in % der sonst üblichen Einsatzmenge einzusparen.

Beispiel 2

Der Versuch von Beispiel 1 wird wiederholt mit der Änderung, daß die Harzmenge auf 2,5 g verringert wird. Die entsprechende Menge 2 n Zitronensäure beträgt 1,66 g. Der Gehalt an freiem Formaldehyd in der Kapseldispersion beträgt 0,2 Masseanteile in %.

Das so verkapselte Parfümöl wird in einer Öl-in-Wasser-Emulsion in einer Maske verarbeitet.

Rezeptur:	
	75,5% Wasser
	0,3% Vaseline
	3,5% Lanolin
	12,5% Emulgator
	0,2% Konservierungsmittel
	2,2% Propylenglykol
	1,0% Sesamöl
	1,0% Vitamin E
	1,0% Vitamin A
	0,1% verkapselte Parfümöldispersion

Die Einarbeitung erfolgt wie in Beispiel 1.

Beispiel 3

Die Versuche von Beispiel 1 und 2 wurden wiederholt und dahingehend variiert, daß die Emulgierung der 30g Lösung des Parfümöls in einer Mischung aus 50 ml Wasser und 10g einer 10%igen wäßrigen Lösung von Gelatine erfolgt. Es wurden unterschiedliche Mengen Aminoharz in Kombination mit Gelatine und 2n Zitronensäure eingesetzt. Günstig war der Anteil von 3g Harz I und 2,0 ml 2n Zitronensäure. Der Gehalt an freiem Formaldehyd in der Kapseldispersion wurde mit 0,15 Masseanteilen in % ermittelt.

Das nach diesem Beispiel verkapselte Parfümöl wurde in einer Tagescreme, die eine Wasser-in-Öl-Emulsion darstellt, eingesetzt.

Rezeptur: 7,5% Kokosfettisoctylester
2,5% Propylenglykol
0,3% Konservierungsmittel
3,5% Farben
0,2% verkapselte Parfümöl-Dispersion
3,5% Emulgator
82,5% Wasser

Die Farbe wird der Wasserphase zugesetzt und gut dispergiert. Die Einarbeitung erfolgt wie in Beispiel 1.

Beispiel 4

76ml Wasser, 15g 10%ige Gelatinelösung, 45g Parfümöl und 4,5g Harz I werden unter hoher Scherung gerührt, auf 60°C erwärmt und bei Erreichen der Temperatur mit 3ml 2n Zitronensäure versetzt. Es werden weitere 5min unter hoher Scherung gerührt, anschließend unter niedriger Scherung 4 Stunden bei 60°C gehalten.

Es werden trockenfesten Mikrokapseln mit einem mittleren Durchmesser von 15,8µm erhalten. Der Gehalt an freiem Formaldehyd in der Kapseldispersion beträgt 0,17 Masseanteile in %. Dieser Ansatz eignet sich für die Herstellung einer Parfümemulsion.

Rezeptur: 64,3–75,8% Wasser
12,3% Emulgatoren
2,0% Silikonöl
4,2% Wollfett
5,5–15,0% verkapselte Parfümöl-Dispersion
0,2% Konservierungsmittel

Die Herstellung erfolgt durch Vermischen der Komponenten und anschließendem Einarbeiten der verkapselten Parfümöl-Dispersion.

Beispiel 3

15g einer 10%igen wäßrigen Lösung von Gelatine werden in 90 ml Wasser bei 40°C unter hoher Scherung nacheinander 45g Pomeranzöl, 4,5g Harz von Typ II und 3 ml 2n Zitronensäure zugesetzt. Nach 5min Rühren unter hoher Scherung bei 40°C wird die Mischung bei 40°C weitere 4 Stunden gerührt.

Die entstandene Mikrokapseldispersion enthält 0,12 Masseanteile in % freien Formaldehyd.

Die so hergestellte verkapselte Parfümöl-Dispersion wird in einem Gesichtspuder verarbeitet.

Rezeptur: 84,0% Talkum
10,0% Kaolin
2,4% Magnesiumstearat
1,5% Bindemittel
2,0% Farbpigmente
0,1% verkapselte Parfümöl-Dispersion

Die verkapselte Parfümöl-Dispersion wird der fertigen Pudermischung bei Zimmertemperatur vorsichtig untergemischt und anschließend appliziert.

Beispiel 6

60 ml Wasser und 10g einer 10%igen Lösung von Gelatine werden gut vermischt, der Mischung nacheinander 3g Harz I und 30g Parfümöl zugesetzt. Unter Rühren unter hoher Scherung wird die Mischung auf 60°C erwärmt und 2 ml 2n Zitronensäurelösung zugesetzt. Nach 10min Rühren unter starker Scherung wird für 5 Stunden bei 65°C weitergerührt. Die entstehende Kapseldispersion weist einen Gehalt an freiem Formaldehyd von 0,12 Masseanteilen in % auf.

Diesmal wird die Parfümöl-Dispersion in ein Lidpuder eingearbeitet.

Rezeptur: 70,0% Talkum
10,0% Kaolin
4,0% Stearate
2,0% Bindemittel
3,9% Farbpigmente
10,0% Glanzpigmente
0,1% verkapselte Parfümöl-Dispersion

Die Verarbeitung erfolgt wie in Beispiel 5.

Beispiel 7

60ml Wasser, 30g Parfümöl und 3,0g Harz werden unter hoher Scherung gerührt, auf 60°C erwärmt und bei Erreichen der Temperatur mit 2,0 ml 2n Zitronensäure versetzt. Es werden weitere 5min unter hoher Scherung gerührt, anschließend unter niedriger Scherung 1h bei 60°C gehalten.

Der Mikrokapseldispersion werden 15 ml 10%ige Gelatinelösung zugesetzt und weitere 3h bei 60°C gehalten. Die Kapseldispersion hat einen Gehalt an freiem Formaldehyd von 0,1 Masseanteilen in %.

Abschließend soll die Verwendung des verkapselten Parfümöls in Tensidmischungen, wie Shampoos, Duschbäder oder Schaumbäder beschrieben werden.

Rezeptur: 40,5% Wasser
22,0% Fettalkoholsulfat
25,2% Sulfobetaine
0,3% Konservierungsmittel
1,5% Weizenkeimöl
0,5% verkapselte Parfümöl-Dispersion

Der fertigen Tensidmischung wird bei Zimmertemperatur unter langsamem schonendem Rühren die Parfümöl-Dispersion zugesetzt und verteilt.

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⑤④ **Perfume particles for use in cleaning and conditioning compositions.**

⑤⑦ Perfume particles are disclosed comprising perfume dispersed within certain water-insoluble polymeric carrier materials. Cleaning and conditioning compositions comprising these perfume particles are also disclosed. The perfume particles allow for preservation and protection of perfumes which are susceptible to degradation or loss in storage and in harsh cleaning conditions. The particles further allow for efficient delivery of a large variety of perfume types to fabrics or other surfaces.

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PERFUME PARTICLES FOR USE IN CLEANING AND CONDITIONING COMPOSITIONS

Technical Field

Perfume particles are disclosed which comprise perfume dispersed within a water-insoluble low molecular weight polymeric carrier material. Cleaning and conditioning compositions having said particles incorporated therein are also disclosed.

Background of the Invention

This invention is based on the concept of controlled perfume release, i.e., perfume release at a time and under conditions that will achieve the desired perfume effect. In general, this is a very old idea, and various methods for achieving this end have been developed, from the simple idea of putting perfume in wax candles to the complex technology of microencapsulation.

One aspect of the concept of controlled release of perfume is providing slow release of perfume over an extended period of time. This is generally achieved by blending perfume with a substance that will, in essence, "trap" the perfume so that small amounts of perfume are released over time. The use of high molecular weight polymeric substances having perfume incorporated therein to provide controlled release of perfume over time is known. See, for example, U.S. Patent 4,184,099 Lindauer et al, issued January 15, 1980; European Patent Application 0 028 118, Leonard, published May 6, 1981; and U.S. Patent 4,110,261, Newland, issued August 29, 1978, which teach combining perfume with a release controlling medium and forming the combination into a solid product for air freshening.

Textile laundering, is also concerned with controlled release of perfumes. Application of this concept allows for slowing down or preventing release of perfume through long periods of shelf storage. Such a concept also allows for using much lower levels of perfume in product since much less perfume is wasted.

Perfume preservation over storage times can be achieved in a variety of ways. The perfume can be made a part of the package for the composition. The perfume can be combined with plastic used to make a bottle, or the perfume can be mixed with a polymer substance and the product used to coat a cardboard package composition, as is disclosed in U.S. Patent 4,540,721, Staller, issued September 10, 1985. Either way the perfume is released over time from the polymer matrix.

The perfume controlled release agent may also be in the form of particles mixed into the laundry composition. One method taught to achieve this end is combining the perfume with a water-soluble polymer, forming into particles and adding to a laundry composition, as is described in U.S. Patent 4,209,417, Whyte, issued June 24, 1980; U.S. Patent 4,339,356, Whyte, issued July 13, 1982; and U.S. Patent 3,576,760, Gould et al, issued April 27, 1971.

The perfume may also be adsorbed onto a porous carrier material, which may be a polymeric material. See, for example, U.K. Patent Publication 2,066,839, Bares et al (applied for in the name of Vysoka Skola Chemicko Technologika), published July 15, 1981. These methods may also be used to mask unpleasant odors in a composition or to protect perfume from degradation by harsh components in a laundry composition. Such methods will provide these benefits only for dry powder or granular type compositions because, as soon as the polymer is hydrated the perfume is released. Thus, these methods provide for perfume fragrance benefits upon opening of the product package and loading into the washing apparatus. While these benefits are desirable, it would be even more desirable to have a method which allows for delivery of undiluted, undissipated and unaltered perfume to fabric and release of the perfume at the end of the laundry process so that the fabric is scented with the desirable perfume odor.

Of course, one method for achieving this end is putting the perfume into a product which goes directly into the dryer. This way, the perfume is delivered to the fabric in the dryer cycle. Such a method is taught in both U.S. Patent 4,511,495, Melville, issued April 16, 1985, and U.S. Patent 4,636,330, Melville, issued January 13, 1987. Both teach forming perfume into particles with a carrier. These particles are then formulated into a composition which is applied to textiles prior to putting into the dryer or prior to clothes-line drying.

An even more desirable method for delivering perfume to laundered fabric would be one which provides for protection of the perfume through the washing process and hence delivery of the perfume to fabric in essentially its original state.

Such a method must allow for prevention of dilution, degradation or loss of the perfume during the wash cycle of the laundry process. This is done by utilizing a system that releases the perfume in the drying process or later after the perfume has been delivered to the fabric. Preventing release of perfume during the washing process involves very different and more difficult technology. Such protection must be stable in
 5 not only the heat-elevated conditions of the wash but must also be stable against degradation by water and other harsh chemicals in the washing process such as bleach, enzymes, surfactants, etc.

One method which has been developed to provide these benefits is perfume microencapsulation. Here the perfume comprises a capsule core which is coated completely with a material which may be polymeric. U.S. Patent 4,145,184, Brain et al, issued March 20, 1979, and U.S. Patent 4,234,627, Schilling, issued
 10 November 18, 1980, teach using a tough coating material which essentially prohibits the diffusion out of the perfume. The perfume is delivered to fabric via the microcapsules and is then released by rupture of the microcapsules such as would occur with manipulation of the fabric.

A more desirable method would involve providing protection of perfume through the wash cycle and release of perfume in the heat-elevated conditions of the dryer. U.S. Patent 4,096,072, Brock et al, issued
 15 June 20, 1978, teaches a method for delivering fabric conditioning agents to textiles through the wash and dry cycle via particles containing hydrogenated castor oil and a fatty quarternary ammonium salt. Perfume may be incorporated into these particles. However, it is not clear whether the perfume thus incorporated is released in the wash cycle or, more desirably, carried in the particles to the dryer and released there, as the particles soften.

U.S. Patent 4,402,856, Schnoring et al, issued September 6, 1983, teaches a microencapsulation technique which involves the formulation of a shell material which will allow for diffusion of perfume out of the capsule only at certain temperatures. This allows for maintenance of the perfume particles through storage and additionally through the wash cycle. The particles adhere to the fabric and are carried over to the dryer. Diffusion of the perfume out of the capsules then occurs only in heat-elevated conditions of the
 25 dryer. These particles are made of gelatin, an anionic polymer and a hardening agent.

U.S. Patent 4,152,272, Young, issued May 1, 1979, teaches incorporating perfume into wax particles to protect the perfume through storage in dry compositions and through the laundry process. The perfume then diffuses through the wax matrix of the particles on the fabric in the heat-elevated conditions of the dryer.

It would be desirable to provide compositions comprising perfume particles that can be incorporated in liquid as well as dry granular or powder compositions and provide long-term storage stability.

It would be desirable to provide a method for delivering a broad range of perfume materials to fabric or other surfaces during the cleaning process.

It would be most desirable to have a perfumed cleaning or conditioning composition which would
 35 provide improved product odor, improved odor of perfume released during the cleaning process, and improved odor and intensity of perfume delivered to the surface being cleaned.

Summary of the invention

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The present invention relates to perfume particles having an average size of less than about 350 microns (preferably an average size not greater than 150 microns, especially particles in the 40-150 micron average size range) which comprise from about 5% to about 70% of a perfume dispersed in from about
 45 30% to about 95% of a water-insoluble polymeric carrier material having a molecular weight of from about 100 to about 30,000, a melting point of from about 37°C to about 190°C, and a hardness value of from about 0.1 to about 15.0.

The present invention further relates to detergent compositions comprising from about 1% to about 90%, preferably from about 5% to about 50%, more preferably from about 10% to about 40%, of a
 50 surfactant selected from the group consisting of anionic, nonionic, zwitterionic, ampholytic, cationic surfactants and mixtures thereof, and an amount of the perfume particles as described above so that the detergent composition comprises from about 0.001 to about 10%, preferably from about 0.1% to about 3.0%, perfume.

The present invention further relates to conditioning compositions comprising from about 1% to about
 55 90%, preferably from about 1% to about 50%, more preferably from about 3 to about 35%, of a conditioning agent selected from the group consisting of cationic softeners; and an amount of the perfume particles as described above so that the conditioning composition comprises from about 0.001% to about 10%, preferably from about 0.1% to 3.0%, perfume.

Detailed Description of the Invention

The present invention allows for preservation, protection, and delivery of perfumes contained in cleaning
 5 and conditioning compositions through extended storage and harsh cleaning conditions. This is achieved by
 isolation of the perfume in a carrier material in the form of small particles. The individual components of the
 invention will now be discussed in detail.

10 The Particles

The perfume particles of the present invention comprise perfume dispersed in certain carrier materials.

In the context of this specification, the term "perfume" means any odoriferous material or any material
 which acts as a malodor counteractant. In general, such materials are characterized by vapor pressure
 15 greater than atmospheric pressure at ambient temperatures. The perfume or deodorant materials employed
 herein will most often be liquid at ambient temperatures, but also can be solids such as the various
 camphoraceous perfumes known in the art. A wide variety of chemicals are known for perfumery uses,
 including materials such as aldehydes, ketones, esters and the like. More commonly, naturally occurring
 plant and animal oils and exudates comprising complex mixtures of various chemical components are
 20 known for use as perfumes, and such materials can be used herein. The perfumes herein can be relatively
 simple in their composition or can comprise highly sophisticated, complex mixtures of natural and synthetic
 chemical components, all chosen to provide any desired odor.

Typical perfumes herein can comprise, for example, woody/earthy bases containing exotic materials
 such as sandalwood oil, civet, patchouli oil and the like. The perfumes herein can be of a light, floral
 25 fragrance, e.g., rose extract, violet extract and the like. The perfumes herein can be formulated to provide
 desirable fruity odors, e.g., lime, lemon, orange and the like. Suitable perfumes include musk ambrette,
 musk ketone, musk tibetine, musk xylol, aurantol, ethyl vanillin and mixtures thereof.

Perfume materials such as these are described more fully in S. Arctander, Perfume Flavors and
Chemicals, Vols. I and II, Aurther, Montclair, N.J., and the Merck Index, 8th Edition, Merck & Co., Inc.
 30 Rahway, N.J., both references being incorporated herein by reference.

In short, any chemically compatible material which exudes a pleasant or otherwise desirable odor can
 be used in the perfumed particles herein to provide a desirable odor when applied to fabrics.

Perfumes which are normally solid can also be employed in the present invention. These may be
 admixed with a liquefying agent such as a solvent prior to incorporation into the particles, or may be simply
 35 melted and incorporated, as long as the perfume would not sublime or decompose upon heating.

The invention also encompasses the use of materials which act as malodor counteractants. These
 materials, although termed "perfumes" hereinafter, may not themselves have a discernible odor but can
 conceal or reduce any unpleasant odors. Examples of suitable malodor counteractants are disclosed in U.S.
 Patent No. 3,102,101, issued August 27, 1963, to Hawley et al.

The perfume particles of the present invention can comprise perfumes which are not typically used to
 deliver a fragrance to a surface, such as fabric through the laundry process. Perfume materials which are
 very volatile, unstable, or soluble in the particular compositions being used to deliver the perfume may be
 used in the present invention because the perfume is isolated from the composition in the particles.
 Perfume materials which are not substantive to fabrics in the laundry process can also be used in the
 40 present invention since the particles deliver the perfume to the fabric surface where it is released. Thus, use
 of the present invention to deliver a perfume to a surface, broadens the class of perfume materials that can
 be utilized.

Generally, the perfume particles of the present invention will comprise from about 5% to about 70%,
 preferably from about 5% to about 50%, perfume. The exact amount of perfume used in the particles will
 50 vary greatly depending on the strength of the particular fragrance used, and the desired odor effect.

The carrier materials of the perfumed particles must meet certain criteria to be useful in the present
 invention. First, the material must be a water-insoluble polymeric material. Further, the material must have a
 molecular weight between about 100 and about 30,000, preferably between about 500 and about 5000.
 Molecular weight of the material may be determined by any standard means. The material must also have a
 55 melting point of between about 37°C and about 190°C, typically 37°C-130°C. This will prevent melting of
 the particles in storage or the washing machine in laundry applications. (It is most desirable to have a
 carrier material that will not completely melt in an automatic dryer, to avoid blocking of the lint screen and
 excessive build-up of heat in the dryer). The melting point of the carrier material should also not be higher

than a point at which the perfume to be combined therewith will decompose. The melting point of the carrier material is measured by what is called the drop melting point method. American Society for Testing and Materials (ASTM) Test Method D127-63 (reapproved 1982, incorporated by reference herein). Briefly, this method involves the following. The sample to be measured is deposited onto a thermometer bulb by
 5 dipping a chilled thermometer into the melted sample. The thermometer bearing the sample is then placed into a test tube and heated by means of a water bath until the sample melts and the first drop falls from the thermometer bulb. The average of the temperatures at which the drops of sample fall is the drop melting point of the sample.

The polymeric material must also be of a particular hardness. This hardness value may be measured
 10 by the standard test method for needle penetration of petroleum waxes. ASTM Test Method D1321-86 (incorporated by reference herein). Briefly, this method involves first melting and further heating the sample to be tested to 17°C (30°F) above its congealing point. The sample is then poured into a container and air cooled under controlled conditions. The sample is then conditioned at the test temperature in a water bath. Penetration is then measured with a penetrometer, which applies a standard needle to the sample for five
 15 seconds under a load of 100 grams. The penetration or hardness value is the depth, in tenths of a millimeter, to which the standard needle penetrates into the wax under these defined conditions. The hardness value of the carrier material must be between about 0.1 and about 15, preferably between 0.1 and 8, to be useful in the present invention. This will allow for particles of a hardness that will optimize the perfume protection/preservation in the carrier.

20 The carrier material must also be inert to the perfume and relatively odorless. The material must allow for diffusion of the perfume therethrough. The carrier material must also be such that it melts without decomposition.

Nonlimiting examples of useful carrier materials include polyethylenes, polyamides, polystyrenes, polyisoprenes, polycarbonates, polyesters, polyacrylates, vinyl polymers and polyurethanes and mixtures
 25 thereof, which meet the above-described criteria, e.g., they are water-insoluble, have a molecular weight between about 100 and about 30,000, have a melting point between about 37°C and 190°C and a hardness value between 0.1 and 15.

One carrier material which meets all of these specified criteria is sold under the trade name POLYWAX 2000 by Petrolite Specialty Polymers Group. This material is a polyethylene having a molecular weight of
 30 about 2,000, a melting point of about 259°F (126°C), and a hardness value (as measured above) at 77°F (25°C) of about 0.5. Another material which meets these criteria is POLYWAX 1000 (also sold by Petrolite Specialty Polymers Group). This material is also a polyethylene having a molecular weight of about 1,000, a melting point of about 237°F (114°C), and has a hardness value at 77°F (25°C) of about 1.0. Another such material is POLYWAX 500.

35 It may be desirable to utilize a mixture of different carrier materials in the perfume particles of the present invention, for example, a blend of a polymeric material and a minor amount of a wax material. Examples of useful wax materials include the materials sold under the trade names BOLER 1014, STARWAX 100, and VICTORY, all available from the Boler Petroleum Company. Such a blend might allow for better deposition properties because the particles formed therefrom would have a "stickier" surface. A
 40 great number of combinations of materials are possible and are intended to be covered by this invention so long as the final blend of carrier materials meets the criteria outlined above.

The choice of carrier material to be used in the perfume particles of the present invention will depend to some degree on the particular perfume to be used. Some perfumes will require a greater amount of protection than others and the carrier material to be used therewith can be chosen accordingly.

45 Generally, the perfume particles of the present invention will comprise from about 30% to about 95%, preferably from about 50% to about 95% carrier material. Again, this will vary with the type and amount of the particular perfume being utilized.

The perfume-containing particles are made as follows. The carrier material is first heated slowly to its melting point. The material is not heated any more than is necessary to just melt the substance. The
 50 perfume is then quickly added, generally as an oil or liquid, at room temperature to the melted carrier substance. The two are quickly mixed into a homogeneous blend then rapidly cooled with liquid nitrogen (or with dry ice or any other means which will cool the mixture quickly) until it has completely solidified. The solid material is then subdivided, generally by grinding or milling, to produce particles of the desired average size. Other methods such as spray cooling or extrusion may also be used to subdivide the
 55 particles.

The perfume particles should be made to have a particle size less than 350 microns. (By "size" herein is meant average particle diameter for substantially spherical particles or the size of the largest diameter or dimension of nonspherical particles. For coated particles, the "size" includes the coating.) Particle sizes

larger than this may be more rapidly lost from the surface they are deposited to and do not provide a relative great enough surface area to release the perfume at the desired rate. Also, particles larger than this may be noticeable on the surface being treated. Particles at the low end of this range, i.e. less than about 100 microns, tend to adhere well to the surface they are delivered to but release the perfume much more readily than larger particles so that the perfume may be dissipated during storage. Additional protection of particles of this size may be necessary to make them useful in the present invention. For example, these smaller particles may comprise polymeric carrier materials which are specially selected to provide additional perfume protection. Additionally, if the particles are incorporated into a liquid composition which has a relatively high viscosity the perfume will not diffuse out of the particles as readily. Finally, the particles may be coated with a material that will slow the rate of diffusion of perfume therethrough.

If the particles to be utilized are not protected via any of these means, preferably the average particle size is larger than 100 microns. Larger particle sizes are more desirably used in compositions such as dry granular detergent compositions, where the larger particle size may help to prevent segregation of the perfume particles from the detergent granules.

The amount of perfume particles used in the compositions of the present invention will depend on the amount of perfume that is desired to be delivered to a particular surface. For example, for laundry detergent and conditioning compositions, generally from about 0.001% to about 10%, preferably from about 0.1% to about 3%, perfume in the product composition is desirable.

To further stabilize particularly volatile perfumes, it may be desirable to preload the perfume (i.e., mix the perfume) onto silica gel or clay prior to combining with the carrier substance. Some perfumes which are not so volatile will not require this special treatment because it would inhibit their release from the carrier substance too much. Optimization of the rate at which the perfume is released from the carrier is the goal, and this additional step allows for better control of that rate with some of the more volatile perfumes.

To further protect the perfume-containing particles in storage, it may be desirable to coat the perfume particles with a material which will prevent the perfume from diffusing out of the particles as readily during long storage periods. This procedure is especially useful when the more volatile perfumes are used, or when particles of a size less than 100 microns are used.

The coating material must be a good film-forming material and it must be inert to the ultimate product composition as well as the perfumed carrier material.

The particles may be coated with more than one coating material to produce a particle having more than one layer of coating material. Different coating materials can be chosen to provide different perfume protection as needed.

The individual perfume-containing particles may also be agglomerated with the coating material to provide larger particles which comprise a number of the individual perfume-containing particles. This agglomerating material surrounding the particles provides an additional barrier to diffusion of the perfume out of the particles. Such an approach also minimizes the surface area of free particles susceptible to perfume diffusion. The ratio of perfume particles to agglomerate material will vary greatly depending upon the extent of additional protection desired. This agglomeration approach may be particularly useful with very volatile perfumes or perfumes that are especially susceptible to degradation. Also, agglomeration of very small perfume particles would provide additional protection against premature diffusion out of perfume.

An alternative approach would involve first coating the individual perfume particles with one coating material and then agglomerating the coated particles with another material. Selection of different coating materials will affect the protection afforded the particles.

Agglomeration of particles in this fashion may also be useful in preventing segregation of small perfume particles from larger detergent granules in a dry granular detergent product.

A wide variety of possibilities exist which will allow for delivery of perfume effect at various times in the cleaning or conditioning process. The less protection provided results in greater perfume effect in product or washing/conditioning process. More protection results in greater perfume effect during the drying process or even later, after the surface has been treated.

Greater protection can be provided by choice of carrier material to be used to form the particles, ratio of perfume to carrier material in the particles, choice of coating material or coating materials (laminar), or agglomeration of particles.

The coating process may be done, for example, with a Wurster fluid bed coater by first making an aqueous solution of the coating material and then contacting the solution with the particles in the fluid bed coater.

Addition of a plasticizer substance to the coating material prior to the coating process will further enhance protection of the perfume-containing particles. The plasticizer will prevent formation of cracks in the coating material over time and helps to prevent the coating material from becoming too brittle.

If the perfume particles are to be incorporated into a dry granular or powder product, the coating material may be water soluble. Such a coating material will protect the perfume particles during storage in product and then may be stripped away when brought into contact with water.

Nonlimiting examples of suitable water-soluble coating materials include such substances as methyl cellulose, maltodextrin, and gelatin. Such coatings can comprise from about 1% to about 25% by weight of the particles. Such coatings can comprise from about 1% to about 25% by weight of the particles.

Nonlimiting examples of plasticizer materials suitable for use with these water-soluble coating materials include glycerin, polyethylene glycol, polypropylene glycol and mixtures thereof; triacetin; triacetin citrate; and lower molecular weight maltodextrins (DE=5); the latter for use with maltodextrin. Generally, the plasticizer material will comprise about 0.5%-10%, by weight of the particles.

For enhanced protection of the perfume particles in a liquid product, it is more desirable to coat the particles with a material that is pH sensitive, i.e., a material that will remain as a coating on the particle in one pH environment but which would be removed from the particle in a different pH environment. For example, such a coating material could be used to coat perfume particles in a liquid fabric softening composition having a pH of about 3. When such a composition is added to the laundry wash water where the pH is greater than 6, the coating material could be stripped away. This would allow for further protection of perfume in liquid compositions over long storage periods, i.e., the perfume would not diffuse out of the particle in the liquid medium as readily. Diffusion of the perfume out of the stripped particle would then take place after the particles were brought into contact with a different pH environment.

Nonlimiting examples of suitable pH-sensitive coating materials include acrylic resins, such as those sold under the trade name EUDRAGIT available from Rohm Pharma, materials sold under the trade name AQUATERIC, available from FMC Corp., and cellulose acetate phthalate and trimellitate, available from Eastman Kodak.

Generally, such pH-sensitive coating materials will comprise from about 5% to about 50%, by weight, of the particles.

Nonlimiting examples of plasticizer materials suitable for use with these pH-sensitive coating materials include diethyl phthalate, tributyl citrate, acetyltributyl citrate, and combinations of propylene glycol or polyethylene glycol with diethyl phthalate (1:1 ratio).

The perfume particles may also be coated with a material that makes the particles more substantive to the surface being treated for example, fabric in the laundry process. Such materials help to deliver the particles to the fabric and maximize perfume release directly on the fabric. Generally, these materials are water-insoluble cationic materials. Examples of useful material include any of the cationic (including imidazolium) compounds listed in U.S. Patent 3,686,025, Morton, issued August 22, 1972, incorporated herein by reference. Such materials are well known in the art and include, for example, the quaternary ammonium salts having at least one, preferably two, C₁₀-C₂₀ fatty alkyl substituent groups; alkyl imidazolium salts wherein at least one alkyl group contains a C₈-C₂₅ carbon "chain"; the C₁₂-C₂₀ alkyl pyridinium salts, and the like.

Preferred cationic softeners useful herein to aid in deposition on fabric include quaternary ammonium salts of the general formula R¹R²R³R⁴N⁺X⁻, wherein groups R¹R²R³ and R⁴ are, for example, alkyl, and X⁻ is an anion, e.g., halide, methylsulfate, and the like, with the chloride and methylsulfate salts being preferred. Especially preferred materials are those wherein R¹ and R² are each C₁₂-C₂₀ fatty alkyl and R₃ and R⁴ are each C₁-C₄ alkyl. The fatty alkyl groups can be mixed, i.e., the mixed C₁₄-C₁₈ tallowalkyl quaternary compounds. Alkyl groups R³ and R⁴ are preferably methyl.

Exemplary quaternary ammonium softeners useful herein include ditallowalkyldimethylammonium methylsulfate, ditallowalkyldimethylammonium chloride, dicoconutalkyldimethylammonium methylsulfate, and dicoconutalkyldimethylammonium chloride.

Generally, these coating materials will comprise from about 1% to about 25% of the perfume particles.

Alternative materials useful for coating the present perfume particles to make them more fabric substantive are described in U.S. Patent 4,234,627, Schilling, issued November 18, 1980, herein incorporated by reference.

Still other coating materials that may be useful for this purpose include silicones and amines.

These types of coating materials may be used alone or in combination with the water-soluble or pH-sensitive coating materials described above to provide a laminated coating.

The perfume particles of the present invention can be incorporated into a wide variety of compositions which deliver a perfume to a surface. One particularly appropriate application is in laundry products. Perfume delivery to fabric through the laundry process is not a simple task. The present invention solves many of the problems generally associated with perfume delivery in this context, e.g., storage stability of perfume in product over extended periods of time or due to incompatibility of perfume with conventional

laundry composition components, such as bleach, enzymes, etc. and dilution or degradation of perfume in the wash process.

6 Cleaning Compositions

The perfumed particles of the present invention may be incorporated in granular or liquid laundry detergent compositions of conventional type. These can contain from about 1% to about 90%, preferably from about 5% to about 50%, more preferably from about 10% to about 40% by weight of organic surfactant selected from anionic, nonionic, zwitterionic, ampholytic, cationic surfactants and mixtures thereof. A typical listing of the classes and species of these surfactants is given in U.S. Patent No. 3,663,961, issued to Norris on May 23, 1972, and incorporated herein by reference.

Suitable synthetic anionic surfactants are water-soluble salts of alkyl benzene sulfonates, alkyl sulfates, methyl ester sulfonates, alkyl polyethoxy ether sulfates, paraffin sulfonates, alpha-olefin sulfonates, alpha-sulfocarboxylates and their esters, alkyl glyceryl ether sulfonates, fatty acid monoglyceride sulfates and sulfonates, alkyl phenol polyethoxy ether sulfates, 2-acyloxy-alkane-1-sulfonate, beta-alkyloxy alkane sulfonate, and soaps.

A particularly suitable class of anionic detergents includes water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium salts or organic sulfuric reaction products having in their molecular structure an alkyl or alkaryl group containing from about 8 to about 22, especially from about 10 to about 20, carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic detergents which may form part of the detergent compositions of the present invention are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8 - C_{18}) carbon atoms produced by reducing the glycerides of tallow or coconut oil and sodium and potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15, especially about 11 to about 13, carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patent No. 2,220,099 and 2,477,383 and those prepared from alkylbenzenes obtained by alkylation with straight chain chloroparaffins (using aluminium trichloride catalysis) or straight chain olefins (using hydrogen fluoride catalysis). Especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl group is about 11.8 carbon atoms, abbreviated as $C_{11.8}$ LAS.

Other anionic detergent compounds herein include the sodium C^{10} - C^{18} alkyl glyceryl ether sulfones, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; and sodium or potassium salts of alkyl phenol ethylene oxide ether sulfate containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain about 8 to about 12 carbon atoms.

Other useful anionic detergent compounds herein include the water-soluble salts of esters of α -sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-1 sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from about 10 to 18, especially about 12 to 16, carbon atoms in the alkyl group and from about 1 to 12, especially 1 to 6, more especially 1 to 4 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from about 12 to 24, preferably about 14 to 16, carbon atoms, especially those made by reaction with sulfur trioxide followed by neutralization under conditions such that any sulfones present are hydrolysed to the corresponding hydroxy alkane sulfonates; water-soluble salts of paraffin sulfonates containing from about 8 to 24, especially 14 to 18 carbon atoms, and β -alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

The alkane chains of the foregoing non-soap anionic surfactants can be derived from natural sources such as coconut oil or tallow or can be made synthetically as, for example, using the Ziegler or Oxo processes. Water solubility can be achieved by using alkali metal, ammonium or alkanolammonium cations; sodium is preferred. Magnesium and calcium are preferred cations under circumstances described by Belgian Patent No. 843,636, Jones et al, issued December 30, 1976. Mixtures of anionic surfactants are contemplated by this invention; a preferred mixture contains alkyl benzene sulfonate having 11 to 13 carbon atoms in the alkyl group or paraffin sulfonate having 14 to 18 carbon atoms and either an alkyl sulfate having 8 to 18, preferably 12 to 18, carbon atoms in the alkyl group, or an alkyl polyethoxy alcohol sulfate having 10 to 16 carbon atoms in the alkyl group and an average degree of ethoxylation of 1 to 6.

Ethoxylated nonionic surfactants materials can be broadly defined as compounds produced by the

condensation of ethylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. In
 5 general, ethoxylated nonionic surfactants suitable herein have an average ethyleneoxy content in the range from about 35% to about 70%, by weight of the surfactant.

Examples of suitable nonionic surfactants include the condensation products of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms in either straight chain or branched chain configuration with from 2 to about 18 moles of alkylene oxide per mole of alcohol. Preferably, the aliphatic alcohol
 10 comprises between 9 and 15 carbon atoms and is ethoxylated with between 2 and 9, desirably between 3 and 8, moles of ethylene oxide per mole of aliphatic alcohol. Such nonionic surfactants are preferred from the point of view of providing good to excellent detergency performance on fatty and greasy soils and in the presence of hardness sensitive anionic surfactants such as alkyl benzene sulfonates. The preferred surfactants are prepared from primary alcohols having no more than about 50% chain branching, i.e., which
 15 are either linear (such as those derived from natural fats or prepared by the Ziegler process for ethylene, e.g., myristyl, cetyl, stearyl alcohols) or partly branched such as the Dobanols and Neodols, which have about 25% 2-methyl branching (Dobanol and Neodol being trade names of Shell) or Synperonics, which are understood to have about 40% to 50% 2-methyl branching. (Synperonic is a trade name of I.C.I.) Specific examples of nonionic surfactants falling within the scope of the invention include Dobanol 45-4, Dobanol 45-
 20 7, Dobanol 45-9, Dobanol 91-3, Dobanol 91-6, Dobanol 91-8, Synperonic 6, Synperonic 9, the condensation products of coconut alcohol with an average of between 5 and 9 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms and the condensation products of tallow alcohol with an average of between 7 and 12 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms. Secondary linear alkyl ethoxylates are also
 25 suitable in the present compositions, for example, those ethoxylates of the Tergitol series having from about 9 to 15 carbon atoms in the alkyl group and up to about 11, especially from about 3 to 9, ethoxy residues per molecule.

Of the above, highly preferred are alkoxyated nonionic surfactants having an average HLB in the range from about 9.5 to 13.5, especially 10 to 12.5. Highly suitable nonionic surfactants of this type are
 30 ethoxylated primary C_9-15 alcohols having an average degree of ethoxylation from about 2 to 9, more preferably from about 3 to 8.

Other useful nonionic surfactants include carbohydrate based surfactants and amine oxides based on olefins.

Suitable ampholytic surfactants are water-soluble derivatives of aliphatic secondary and tertiary amines
 35 in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate or phosphonate.

Suitable zwitterionic surfactants are water-soluble derivatives of aliphatic quaternary ammonium phosphonium and sulfonium cationic compounds in which the aliphatic moieties can be straight chain or
 40 branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water-solubilizing group.

Cationic surfactants that may be used in the detergent compositions of the present invention include coconut trimethylammonium chloride.

The detergent compositions of the invention can also contain from about 1% to about 80%, preferably
 45 from about 5% to about 50%, of detergency builder.

Suitable detergent builder salts useful herein can be of the polyvalent inorganic and polyvalent organic types or mixtures thereof. Non-limiting examples of suitable water-soluble inorganic alkaline detergent builder salts include the alkali metal carbonates, borates, phosphates, polyphosphates, tripolyphosphates and bicarbonate.

60 Examples of suitable organic alkaline detergency builder salts are:

(1) Water-soluble amino polyacetates, e.g., sodium and potassium ethylenediaminetetraacetates, nitrilotriacetates and N-(2-hydroxyethyl)nitrilotriacetates;

(2) Water-soluble salts of phytic acid, e.g., sodium and potassium phytates;

(3) Water-soluble polyphosphonates, including sodium, potassium and lithium salts of ethane-1-
 65 hydroxy-1,1-diphosphonic acid; sodium, potassium and lithium salts of methylenediphosphonic acid and the like.

(4) Water-soluble polycarboxylates such as the salts of lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patents 821,368, 821,369 and 821,370; the materials disclosed in U.S.

Patent 4,663,071, Bush et al, issued May 5, 1987; succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid; citric acid, acconitic acid, citraconic acid, carboxymethyloxysuccinic acid, lactoxysuccinic acid and 2-oxy-1,1,3-propane-tricarboxylic acid; oxydilsuccinic acid, 1,1,2-ethane tetracarboxylic acid, 1,1,3,3-propane tetracarboxylic acid and 1,1,2,3-propane tetracarboxylic acid; cyclopentane-cis, cis, cis-tetracarboxylic acid, cyclopentadienide penta-carboxylic acid, 2,3,4,5-tetrahydrofuran-cis, cis, cis-tetracarboxylic acid, 2,5-tetrahydrofuran-cis-dicarboxylic acid, 1,2,3,4,5,6-hexane-hexacarboxylic acid, mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent 1,425,343.

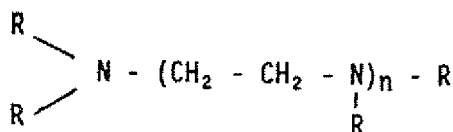
Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in Canadian Patent No. 755,038, e.g., a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate and trisodium ethane-1-hydroxy-1,1-diphosphonate.

A further class of builder salts is the insoluble aluminosilicate type which functions by cation exchange to remove polyvalent mineral hardness and heavy metal ions from solution. A preferred builder of this type has the formulation $\text{Na}_z(\text{AlO}_2)_z(\text{SiO}_2)_y \cdot x\text{H}_2\text{O}$ wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5 and x is an integer from about 15 to about 264. Compositions incorporating builder salts of this type form the subject of British Patent Specification No. 1,429,143, published March 24, 1976, German Patent Application No. OLS 2,433,485, published February 6, 1975, OLS 2,525,778, published January 2, 1976, and U.S. Patent 4,605,509, Corkill et al, issued August 12, 1986, the disclosures of which are incorporated herein by reference.

Another suitable component of the present compositions is a water-soluble magnesium salt which is added at levels in the range from about 0.015% to about 0.2%, preferably from about 0.03% to about 0.15%, and more preferably from about 0.05% to about 0.12%, by weight of the compositions (based on weight of magnesium). Suitable magnesium salts include magnesium sulfate, magnesium sulfate heptahydrate, magnesium chloride, magnesium chloride hexahydrate, magnesium fluoride and magnesium acetate. Desirably, the magnesium salt is added to the compositions as part of the aqueous slurry crutcher mix and is then converted to dry granular form, for instance by spray drying. The magnesium salt can provide additional low temperature stain removal benefits as described in British Patent Application No. 80/15542.

The detergent compositions of the invention can also be supplemented by bleaches, especially sodium perborate tetrahydrate or sodium percarbonate at levels from about 5% to about 50%. Examples of laundry compositions containing bleaching agents which are useful in the present invention are those disclosed in U.S. Patent 4,412,934, Chung et al, issued November 1, 1983; U.S. Patent 4,536,314, Hardy et al, issued August 20, 1985; U.S. Patent 4,539,130, Thompson et al, issued September 3, 1985; and U.S. Patent 4,681,695, Divo, issued July 21, 1987. The perfumed particles of the present composition are particularly useful in such compositions because the perfume is protected from degradation by the bleach.

The compositions of the present invention may also include from about 0.05% to about 0.6% (acid basis), preferably from about 0.06% to about 0.3%, of aminopolyphosphonic acid, or salt thereof, having the general formula:



wherein n is an integral number from 0 to 3, and each R is individually hydrogen or $\text{CH}_2\text{PO}_3\text{H}_2$ provided that at least half of the radicals represented by R are $\text{CH}_2\text{PO}_3\text{H}_2$. Preferred aminopolyphosphonic acids are selected from nitrilotri(methylenephosphonic acid), ethylene-diaminetetra(methylenephosphonic acid), diethylenetriamine(pentamethylenephosphonic acid) and mixtures thereof.

An alkali metal, or alkaline earth metal, silicate can also be present in the compositions of the present invention. The alkali metal silicate is preferably present at from about 3% to about 8%. Suitable silicate solids have a molar ratio of SiO_2 :(alkali metal) $_2\text{O}$ in the range from about 1.0 to about 3.3, more preferably from 1.5 to 2.0. Other suitable ingredients include soil-suspending agents such as the water-soluble salts of carboxymethyl cellulose and of methyl vinyl ether/maleic anhydride copolymer, nonionic cellulose materials such as hydroxyethyl cellulose and polyethylene glycols. Examples of soil release polymer materials suitable for use in the detergent compositions of the present invention are disclosed in U.S. Patent 4,702,857, Gosseink, issued October 27, 1987.

Preferred enzymatic materials for use in the present invention include the commercially available

amylases and neutral and alkaline proteases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in U.S. Patent Nos. 3,519,750, 3,533,139, and 4,767,557. Examples of suitable enzymes include lipase, cellulase and the materials sold under the Registered Trade Marks Maxatase and Alcalase.

5 Examples of bleach activators suitable in the compositions of the invention are organic peroxyacid precursors including esters such as trichloroethyl acetate, acetylacetoxyhydroxamic acid, sodium p-acetoxy benzene sulphonate sodium benzoyl phenol sulphonate, methyl o-acetoxy benzoate and Bisphenol A diacetate; imides such as N-acetyl caprolactam, N-benzene sulphonyl phthalimide, tetraacetylthylenediamine, tetraacetylmethylenediamine, tetraacetylhexamethylenediamine and tetraacetyl-
10 glycouril; imidazoles such as N-acetylbenzimidazole; oximes such as diacetyl dimethyl glyoxime; as well as certain carbonates, guanidines, triazine derivatives; and nonanoyl sodium acyl-oxybenzene sulfonate (also in the bisform).

The detergent compositions of the present invention may also comprise fabric softening agents. Examples of such materials include smectite type clays such as bentonite, polyethylene oxide with a
15 molecular weight of about 500,000,000, and N,N-diallowmethyl amine. Examples of such laundry cleaning and conditioning compositions are disclosed in U.S. Patents 4,141,841, McDonald, issued February 27, 1979, and U.S. Patent 4,762,645, Tucker et al, issued August 9, 1988.

Other optional detergent composition components include halogen bleaches (e.g., sodium and potassium dichloroisocyanurates), soil suspending agents (e.g., sodium carboxymethylcellulose), fabric bright-
20 teners, enzyme stabilizing agents, color speckles, suds boosters or suds suppressors, anticorrosion agents, dyes, fillers, germicides, pH adjusting agents, nonbuilder alkalinity sources, and the like.

To combine the perfumed particles with a granular detergent composition, it is most desirable to coat the particles or agglomerate the particles with a water-soluble inert filler material to achieve particles of the same size as the granules. This will allow for a homogenous combination of the particles and granules and
25 will avoid particle segregation during processing, packaging and shipping. Generally, detergent granules are about 100-1000 microns (average diameter) in size. Suitable water-insoluble inert filler materials include methyl cellulose, malto dextrin, and gelatin. The particles may be coated or agglomerated utilizing a Wurster fluid bed coater by first making an aqueous solution of the agglomerating material and then contacting the solution with the particles in the fluid bed coater.

30 The perfumed particles may be simply mixed into liquid detergent compositions. Examples of suitable liquid laundry detergent compositions for use in the present invention include U.S. Patent 4,490,285, Kebanli, issued December 25, 1984, and U.S. Patent 4,507,219, Hughes, issued March 26, 1985. However, the perfumed particles may first be coated with a pH-sensitive material as disclosed supra, to further prevent premature diffusion of the perfume out of the particles.

35 The preferred particle may also be utilized with a laminated laundry product formed from two plies of water-insoluble tissue, at least one of which is water permeable, which are laminated together. At least one of the plies has cup-like depressions, surrounded by rims, and the other ply being attached to the first ply at the rim to physically separate the cups. Plies of the tissue paper described in U.S. Patent 4,529,480, Trokhan, issued July 16, 1985, may be utilized. Other materials which can be used to form suitable
40 laminates and processes for forming laminates are disclosed in U.S. Patents 4,571,924, Bahrani, issued February 25, 1986, and 4,638,907, Bedenk et al, issued January 27, 1987. Detergent compositions suitable for use with such laminated laundry products are disclosed, for example, in U.S. Patent 4,715,979, Moore et al, issued December 29, 1987.

It may be desirable to also add perfume to the composition, as is, without protection via the particles.
45 Such perfume loading would allow for aesthetically pleasing fragrance of the composition itself. Upon opening the package containing the composition and as the product is added to water, this immediate release of fragrance may be desirable.

This perfume would be added via conventional means, e.g., mixing, as is, into a liquid composition or spraying onto dry product compositions. The protected perfume in the particles provides an additional
50 benefit, i.e., enhanced perfuming of the fabric as it leaves the laundry process.

Typically, for laundry detergent compositions an amount of the perfume particles is incorporated in the composition so as to provide the composition with from about 0.001% to about 10%, preferably from about 0.1% to about 3%, perfume.

55 Use of the perfume particles of the present invention in laundry detergent compositions provides an efficient means for delivery of a wide variety of perfume materials to fabric. Furthermore, such use provides a consistent odor profile across the laundry process, i.e., from product, to wash, rinse and dry cycles to fabric.

The perfume particles of the present invention may also be used in a wide variety of other types of

cleaning products. For example, hard surface cleaning compositions such as those disclosed in U.S. Patents 4,005,027, Hartman, issued January 25, 1977; 3,985,668, Hartman, issued October 12, 1976; 4,414,128, Goffinet, issued November 8, 1983; and 3,679,608, Aubert et al, issued July 25, 1972, incorporated by reference herein, may be utilized with the present perfume particles and are intended to be within the scope of the present invention.

Shampoo compositions may also be utilized with the perfume particles of the present invention. Such compositions are disclosed in U.S. Patents 4,704,272, Oh et al, issued November 3, 1987; 4,741,855, Grote et al, issued May 3, 1988; and 4,345,080, Bolich, Jr., Issued August 17, 1982 (combination shampoo and hair conditioning composition), herein incorporated by reference, and are intended to be within the scope of the present invention.

Dishwashing detergent compositions such as the light-duty liquid detergent compositions described in U.S. Patents 4,133,779, Hellyer et al, issued January 9, 1979; 4,316,824, Pancheri, issued February 23, 1982; and 4,555,360, Bissett et al, issued November 26, 1985, incorporated by reference herein, may also have the perfume particles of the present invention incorporated therein and are intended to be within the scope of the present invention. Granular automatic dishwashing detergent compositions may also be utilized with the present perfume particles. Examples of such compositions are disclosed in U.S. Patents 4,714,562, Roselle et al, issued December 22, 1987, and 3,630,923, Simmons et al, issued December 28, 1971, incorporated by reference herein. Liquid automatic dishwashing detergent compositions such as those described in European Patent Application 201,496, published April 27, 1988, incorporated by reference herein, are also useful in combination with the present perfume particles.

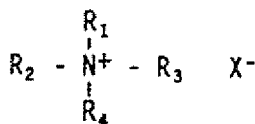
Bar soap compositions may also be utilized with the perfume particles of the present invention. Such compositions are described in U.S. Patents 4,557,853, Collins, issued December 10, 1985; 4,673,525, Small et al, issued June 16, 1987; and 4,714,563, Kajs et al, issued December 22, 1987, all of which are incorporated by reference herein, and are intended to be within the scope of the present invention.

Laundry bleach compositions may also be used with the perfume particles of the present invention, since the perfume is protected from the bleach by the carrier materials. Examples of such compositions are disclosed in U.S. Patent 4,412,934, Chung et al, issued November 1, 1983 (dry granular); British Patent No. 2,188,654, published October 7, 1987; and U.S. Patent 4,100,095, Hutchins, issued July 11, 1978 (liquid), all of which are incorporated by reference herein.

Conditioning Compositions

The perfume-containing particles of the present invention may also be incorporated into fabric conditioning compositions. Such compositions typically contain as active ingredients cationic softeners. The cationic softeners useful in the present fabric softening compositions can be any of those substantially water-insoluble cationic active materials generally recognized in the art for their fabric softening properties. Typical examples are:

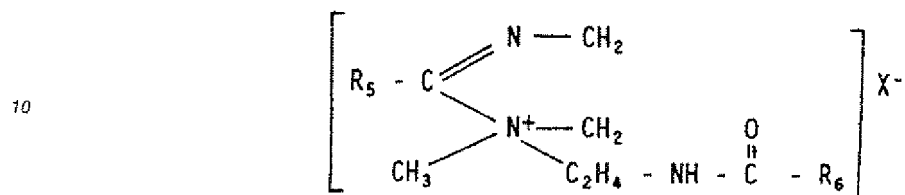
(a) Mono nitrogen quaternary ammonium cationic salts having the structure:



wherein R_1 is selected from C_1 to C_{20} alkyl and alkenyl groups and R_2 is selected from the group consisting of C_{14} to C_{20} alkyl and alkenyl groups and R_3 and R_4 are the same or different from each other and are selected from the group consisting of C_1 to C_3 alkyls or $-(C_nH_{2n}O)_xH$ wherein n is 2 or 3, x is from 1 to about 3, and wherein X^- is halide, HSO_4^- , nitrate, methylsulfate or ethylsulfate. It is preferred that X^- be halide, and the preferred halides are chloride and bromide. Exemplary compounds of this class are: stearyltrimethyl ammonium chloride, myristyltriethyl ammonium bromide, dimyristyldimethyl ammonium chloride, dipalmityldiethyl ammonium bromide, distearyldimethyl ammonium chloride, distearyldimethyl ammonium bromide, distearyldiisopropyl ammonium bromide, diarachyldimethyl ammonium chloride, distearyl-2-hydroxypropylmethyl ammonium chloride, oleylstearyldimethyl ammonium ethylsulfate, distearyl-2-hydroxyethylmethyl ammonium methylsulfate, and dimethyl bis(stearoyl oxyethyl) ammonium chloride, dimethyl alkyl ether ester ammonium quaternary compounds, and dimethyl diisopropyl ester ammonium quaternary compounds. Preferably the R_1 and R_2 groups are derived from tallow and the R_3 and R_4

groups are methyl. The tallow can be hydrogenated or unhydrogenated. Hydrogenated (i.e., saturated) tallow is preferred, and halides are the preferred anions. Accordingly, preferred mono nitrogen quaternary ammonium salt softener compounds herein are dihydrogenatedtallow dimethyl ammonium chloride and dihydrogenatedtallow dimethyl ammonium bromide.

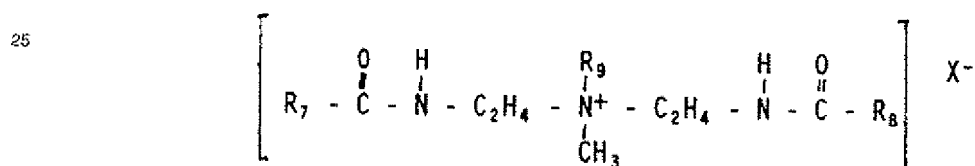
5 (b) Imidazolinium salts of the formula:



75 wherein R₅ and R₆ are the same or different from each other and are selected from the group consisting of C₁₄ to C₂₀ alkyl and alkenyl groups, wherein X⁻ is as defined above.

Exemplary compounds of this type are: 1-methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate, 1-methyl-1-oleylamidoethyl-2-oleylimidazolinium chloride, 1-methyl-1-palmitoleylamidoethyl-2-palmitoleylimidazolinium ethylsulfate, 1-methyl-1-soyaamidoethyl-2-soyaimidazolinium methylsulfate, 1-methyl-1-hydrogenatedtallowimidazolinium methyl sulfate, and 1(2-tallowylaminoethyl)-2 tallowylimidazoline.

(c) Di(2-amidoethyl)methyl quaternary ammonium salts having the structure:



wherein R₇ and R₈ are the same or different from each other and are selected from the group consisting of C₁₄ to C₂₀ alkyl and alkenyl groups, wherein R₉ is selected from H, methyl, ethyl and -(C_nH_{2n}O)_xH wherein n is 2 or 3 and x is from 1 to about 5 (preferably 3), and wherein X⁻ is as defined above. Preferably R₇ and R₈ are alkyl and R₉ is -(C_nH_{2n}O)_xH. This class of compounds is disclosed in U.S. Patent No. 4,134,840, Mineqishi et al. issued January 16, 1979. Incorporated herein by reference.

Exemplary compounds are di(di-hydrogenatedtallowamidoethyl) ethoxylated (2 ethoxy groups) methyl ammonium methylsulfate, di(2-hydrogenatedtallowamidoethyl) dimethyl ammonium ethylsulfate, di(2-palmitylamidoethyl)-2-hydroxyethyl ammonium chloride, di(2-oleylamidoethyl) propoxylated (3 propoxy groups) methyl ammonium bromide, di(2-palmitoleylamidoethyl) dimethyl ammonium ethylsulfate and di(2-stearylamidoethyl) propoxylated (2 propoxy groups) methyl ammonium methylsulfate.

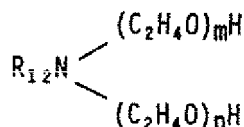
The cationic softener compounds are present in the compositions of the invention at levels of from about 1% to about 50%, preferably from about 3% to about 35%. The softeners can be used singly or in mixtures.

45 Amines may be present in the compositions herein, either as a minor component sometimes present in the cationic softeners which are used, or are purposely added to the compositions to impart some desired property, e.g., for improved emulsification of the cationic softeners, for freeze-thaw recovery (i.e., recovery of the compositions to a homogeneous condition after being frozen), for viscosity control or as supplementary softeners.

50 Generally, the amount of amine present in the compositions herein will be from about 0.05% to about 5%, more typically from about 0.1% to about 2%.

Typical amine components found in cationic fabric softener compositions are dihydrogenatedtallow methyl amines, 1-tallowamidoethyl-2-tallowimidazoline and di(2-hydrogenatedtallowamidoethyl)alkyl ethoxylated amine.

Useful amines for freeze-thaw recovery, emulsification and viscosity control are compounds of the formula:



5

wherein R_{12} is an alkyl or alkenyl group of from about 14 to about 20 carbon atoms and $m + n$ is from about 2 to about 30. A typical commercial material of this class is sold under the name Varonic T-220D by
 10 Sherex Chemical Company.

Diamines are also useful emulsifying and freeze-thaw recovery agents in the compositions herein. (See U.S. Patent No. 4,045,361, Watt et al, issued August 30, 1977, and EPO Application 18039, Clint et al, published October 29, 1980, both incorporated by reference herein.) A typical exemplary diamine is N-talloyl-N,N',N'-tris(2-hydroxyethyl)-1,3-propane-diamine.

15 Typical monoamines which can be used as supplementary softeners include stearyl dimethyl amine, dihydrogenated tallow methyl amine and hydrogenated tallow dimethyl amine.

Materials which are typically used in fabric softener compositions can be optionally used in the compositions of the present invention. These include lower alcohols (e.g., ethanol, isopropanol, etc.), perfumes, dyes, ionizable salts for viscosity control, nonionic fabric softeners (e.g., long-chain hydrocarbons
 20 and fatty glycerides), fatty acids, and polyethylene glycols.

Other ingredients employable in fabric softening compositions can also be included, for example, ironing aids such as silicones or dextrin derivatives, preservatives and bactericides, whether effective to protect the composition or to treat fabrics, soil release polymers (as described above), and the like.

Examples of suitable liquid fabric softening compositions for use in the present invention are those
 25 disclosed in U.S. Patent 3,974,076, Wiersama et al, issued August 10, 1976; U.S. Patent 4,424,134, Sissin et al, issued January 3, 1984; and U.S. Patent 4,661,269, Trinh et al, issued April 28, 1987.

Additional fabric softening articles useful in the present invention are those in the form of a fabric softening composition adhered to an absorbent substrate, such as paper or a woven or non-woven cloth sheet, are disclosed in U.S. Patent 4,073,996, Bedenk et al, issued February 14, 1978; U.S. Patent
 30 3,944,694, McQueary, issued March 16, 1976; and U.S. Patent 4,237,155, Kardouche, issued December 2, 1980.

It may be desirable to also add perfume to the conditioning composition, as is, without protection via the particles. Such perfume loading would allow for aesthetically pleasing fragrance of the composition itself. Upon opening the package containing the composition and as the product is added to water, this
 35 immediate odor impact is desirable.

This perfume would be added via conventional means, e.g., mixing, as is, into a liquid composition or spraying onto dry product compositions. The protected perfume in the particles provides a different benefit, i.e., perfuming the clothes as they leave the laundry process.

Typically, for conditioning detergent compositions an amount of the perfume particles is incorporated in
 40 the composition so as to provide the composition with from about 0.001% to about 10%, preferably from about 0.1% to about 3%, perfume.

Use of the perfume particles of the present invention in fabric softening compositions provides an efficient means for delivery of a wide variety of perfume materials to fabric. Furthermore, such use provides a consistent odor profile from product, through the laundry process, to fabric.

45 The perfumed particles of the present invention may also be used in hair conditioning compositions and conditioning shampoo compositions such as those disclosed in U.S. Patent 4,764,363, Bolich, issued August 16, 1988, and European Patent Publications 205,306, published December 17, 1986 and 240,350, published October 7, 1987. Such compositions are intended to be within the scope of the present invention.

50

Method of Use

During the washing or conditioning process, the perfume particles are delivered to the surface to be perfumed. Thereafter the perfume will diffuse out of the particles and give the surface the desired fragrance
 55 impart.

In the laundry process, the perfume particles adhere to the fabric being laundered as they contact it. When the laundered fabrics are transferred to a clothes dryer or line dried the perfume is believed to diffuse out of the particles in a substantially unaltered state, thus delivering an enhanced perfume to the

fabric.

The following examples illustrate the present invention. It will be appreciated that other modifications of the present invention, within the skill of those in the laundry composition formulation art, can be undertaken without departing from the spirit and scope of this invention.

5 All parts, percentages, and ratios herein are by weight unless otherwise specified.

Example I

10

The perfume particles useful in laundry compositions of the present invention are prepared as follows:

Twenty-five grams of POLYWAX 2000 (polyethylene having a molecular weight of 2000) is heated in a beaker on a hot plate at about 130 °C just until melted. 8.33 Grams of perfume at room temperature is added to the melted POLYWAX and the mixture remains in the fluid state.

15 An Osterizer Blender with a custom made stainless steel cylindrical vessel which is about 7 cm in diameter, about 10 cm in height, about 0.5 cm thick, and completely enclosed except for a pinhole in the top to allow for release of nitrogen is used to grind the solid POLYWAX perfume into particles. The blender container is first chilled with liquid nitrogen. The melted POLYWAX/perfume is quickly mixed and then poured into the blender container, and more liquid nitrogen is added to quickly chill/harden the
20 POLYWAX/perfume mixture.

The blender is set on its highest speed, and the solid POLYWAX/perfume is ground for 30 seconds. The top and sides of the blender container are tapped to knock the particles back down to the bottom of the blender container, and the solid POLYWAX/perfume is ground again at high speed for 30 seconds.

The particles may be washed with methanol to clean from the particle surfaces unincorporated perfume
25 which may make the particle surfaces too sticky. About 100 ml of methanol per 40 grams of particles is generally sufficient. Suction filtration is used to remove excess methanol from the particles, and the particles preferably are permitted to additionally stand in open air to allow any remaining methanol to evaporate.

The particles may be sieved to obtain particles in the most desirable size range. Sieves having 250 and
30 125 micron openings may be used to obtain particles primarily in the 125 to 250 micron size range.

Particles thus sieved are about 80% in the 125 to 250 micron size range. These particles may be added to conventional laundry products to provide the compositions with a level of perfume of from about 0.1% to about 3.0%. The particles allow for protection of the entrapped perfume through the laundry process. The particles adhere to the laundered textiles and are carried into the dryer. As textiles are dried in
35 a heat elevated environment, the perfume diffuses out of the particles. This released perfume is essentially unaltered from its original state.

If a particularly volatile perfume is used to make the perfume particles, the perfume may be mixed with silica gel prior to mixing with the melted POLYWAX 2000. The ratio of perfume to silica gel may be about 80:20. After the perfume and silica gel are combined, it is most desirable to allow the combination to stand
40 (covered) for several hours before combining with the melted POLYWAX. The perfume/silica gel is desirably mixed with the melted POLYWAX 2000 at a ratio of about 1:2.3.

Example II

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Perfume particles that provide additional protection for use in liquid compositions are prepared as follows. The particles of Example I are coated with an amount of the acrylic resin EUDRAGIT (available from Rohm Pharma) sufficient to comprise 12%, by weight, of the particles. The coating process is accomplished
50 utilizing a Wurster fluid bed coater by first making an aqueous solution of the coating material and then contacting the solution with the particles in the fluid bed coater for a time sufficient to deposit the desired amount of coating material to the particles. The plasticizer substance diethyl phthalate may be combined with the pH-sensitive coating material prior to the coating process to provide a more durable coating to the particles. The plasticizer is added in an amount sufficient to comprise 1%, by weight of the particles.

55 These coated perfume particles will provide additional protection against diffusion of perfume out of the particles through extended storage periods in the liquid composition. When the particles are introduced into an environment having a different pH, the coating may be stripped away and the perfume will diffuse out of the particles and provide the fragrance benefit.

Example III

The following is a bleach-containing granular laundry detergent composition:

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Component	Weight %
Sodium C ₁₃ alkylbenzene sulfonate	7.5
Sodium C ₁₄₋₁₅ alkylsulfate	7.5
C ₁₂₋₁₃ alkyl polyethoxylate (6.5) stripped of unethoxylated alcohol and lower ethoxylate	2.0
C ₁₂ alkyltrimethyl ammonium chloride	1.0
Sodium tripolyphosphate	32.0
Sodium carbonate	10.0
Sodium perborate monohydrate	5.3
Sodium octanoyloxybenzene sulfonate	5.8
Sodium diethylene triamine pentaacetate	0.5
Sodium sulfate, H ₂ O and minors	Balance

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The above composition is prepared using conventional means. The composition is combined with the perfume particles of Example I as follows. An amount of the perfume particles of Example I is combined with the detergent composition so that the detergent composition comprises about 0.3% perfume (about 1-1/2% of the detergent composition will comprise the perfume particles).

25

The particles may be simply mixed in with the detergent granules. To prevent segregation of the perfume particles during packaging and shipping (due to their smaller size relative to the detergent granules), the particles may be coated or agglomerated with a water-soluble coating material prior to combining with the detergent granules. This can be accomplished with a Schugi mixer (Flexomix 160) where a sufficient amount of a dextrin glue solution (2% dextrin, 3% water) is sprayed onto the particles to result in agglomerates of perfume particles in the same size range as other detergent granules.

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The perfume is protected in the particles from degradation by the bleach in the detergent composition over long periods of storage. When used in the laundry process this detergent composition will provide perfume fragrance in substantially its original state from product, through the wash process to fabric.

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A great number of perfumes can be utilized in the present composition that would not otherwise be appropriate for use in such laundry detergent compositions.

Example IV

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Granular laundry detergent compositions of the present invention are prepared as follows:

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Component	Weight %				
	A	B	C	D	E
C ₁₂ alkylbenzene sulfonate (sodium)	6.8	7.0	10.0	5.6	5.9
Tallow alcohol sulfate (sodium)	-	-	3.0	2.4	2.5
Tallow alcohol polyethoxylate(EO11)	0.9	0.9	1.0	0.4	0.3
Fatty alcohol (C ₁₂₋₁₅) polyethoxylate(7)	-	-	2.0	5.8	5.0
Cetyl dimethyl amineoxide	0.4	0.5	-	-	-
Hydrogenated fatty acid	0.2	0.3	1.0	-	-
Sodium tripolyphosphate	22.0	-	24.0	24.0	-
Zeolite 4A	-	21.0	-	5.4	20.5
Sodium nitrilotriacetate	-	3.0	4.0	-	-
Sodium carbonate	10.0	7.0	-	13.5	12.8
Sodium perborate (1 aq.)	2.0	-	-	14.0	2.0
Sodium perborate (4 aq.)	11.0	15.0	-	-	13.0
TAED	1.0	1.2	-	5.3	2.1
C ₁₂ alkyl trimethyl ammonium chloride	1.5	1.9	-	-	-
Distearyl methylamine	2.5	3.1	-	-	-
Sodium silicate (SiO ₂ /Na ₂ O = 1.6)	7.1	3.0	8.0	7.7	2.9
Carboxymethylcellulose	0.3	0.4	0.8	-	0.3
Copolymer maleic/acrylic acid (70/30 MW 40000-80000)	2.0	1.0	1.0	2.6	-
Na-polyacrylate (MF 1000-10000)	-	2.0	1.0	1.0	3.9
Sulfonated zinc phthalocyanine	30ppm	-	25ppm	40ppm	-
EDTA	0.2	0.2	0.4	0.5	0.3
Ethylenediamine tetramethylene phosphonic acid (Na salt)	0.1	0.3	0.1	0.2	0.3
Enzymes (protease, amylase, cellulase, lipase)	0.4	0.8	0.6	1.6	0.8
Optical brightener	0.2	0.2	0.3	0.2	0.2
Silicone/silica suds suppressor	0.7	0.5	0.6	0.5	0.4
Smectite clay	8.0	6.5	-	-	-
Sulfate, minors, water	Balance to 100%				

The above compositions are prepared using conventional means. The composition is combined with the perfume particles of Example I as follows. An amount of the perfume particles is added to the above compositions so that about 2% of the composition comprises the perfume particles. The particles are simply mixed into the detergent composition, or they may be coated or agglomerated to achieve somewhat larger particle size to prevent segregation of the particles out of the composition during shipping, etc.

The perfume is protected in the particles from degradation or dissipation over long periods of storage. When used in the laundry process, this detergent composition will provide perfume fragrance in substantially its original state from product, through the wash process and onto the fabric.

Example V

A laundry detergent and conditioning composition is prepared as follows:

Component	Weight %
Dimethyl di-hydrogenated tallow ammonium chloride (95% active powder)	75
Tallow alcohol	25
	100

The dimethyl di-hydrogenated tallow ammonium chloride (DTDMAC) and tallow alcohol are melted together to form a clear solution at 250 ° F. This molten solution is atomized at 1600 psi into a chamber with

ambient temperature air passing through the chamber. The atomized droplets freeze into solid particles in the size range of about 20 microns to about 150 microns. The softening point of the DTDMAC/tallow alcohol mixture is about 165° F. The DTDMAC/tallow alcohol mixture has a solubility of substantially less than 10 ppm in 25° C water.

5 Sodium tripolyphosphate (STP) is then mixed with the DTDMAC/tallow alcohol prills in a 4:7 ratio of polyphosphate:prill. The sodium tripolyphosphate is a dry, anhydrous powder with at least 90% passing through a 100-mesh Tyler sieve. The 7:4 ratio DTDMAC/tallow alcohol prill:sodium tripolyphosphate (STP) mixture is fed into a Schugi mixer (Flexomix 160) where about 5 parts dextrin glue solution (1.67 parts dextrin, 3.33 parts water) is sprayed onto the mixture. This results in agglomerates of prill-STP in the same
10 size range as other detergent granules, about 150 to 1190 microns.

The 16 parts prill-STP agglomerates are then discharged from the Schugi Flexomix 160 mixer and mixed with about 12 parts of sodium montmorillonite clay of good fabric softening performance and having an ion exchange capacity of about 63 meq/100 g (available from Georgia Kaolin Co. U.S.A. under the trade name Brock). The resulting mix is aged for approximately one hour and then mixed with 0.4 parts of silica
15 to increase flowability. The total admix comprises 7 parts DTDMAC/tallow alcohol prill, 4 parts STP, 5 parts dextrin glue solution, 12 parts sodium montmorillonite clay and 0.4 parts silica, resulting in a 28.4 part admix to detergent granules.

The particulate detergent additive is incorporated into a detergent composition as follows:

20	Component		Weight %	
	Sodium C ₁₁₋₁₃ alkylbenzene sulfonate		7.70	71.6%
25	Sodium tallow alkyl sulfate		4.23	
	Sodium C ₁₄₋₁₆ alkyl triethoxy sulfate		4.23	
30	Sodium tripolyphosphate		19.25	
	Sodium silicate (2.0 ratio)		11.55	
35	Sodium sulfate		19.25	
	Water		3.85	
40	Miscellaneous (perfume, brightener, etc.)		<u>1.54</u>	
	Subtotal Weight %			
	Plus the particulate detergent admix:			
45	Sodium montmorillonite		12.0%	28.4%
	Silica		0.4%	
	AGGLOMERATE			
50	Sodium tripolyphosphate		4.0%	28.4% 100.0%
	DTDMAC/tallow alcohol prill		7.0%	
55	Dextrin glue solution		<u>5.0%</u>	
	Subtotal Weight %			
	TOTAL Weight %			<u>28.4%</u> <u>100.0%</u>

The above composition is combined with the perfume-containing particles of Example I as follows. An amount of the perfume particles of Example I is combined with the combination detergent and conditioning composition so that the composition comprises about 0.6% perfume (about 2-1/2% of the detergent composition will comprise the perfume particles). The particles may be simply mixed into the detergent and conditioning granules or may be agglomerated with a water-soluble material to provide agglomerates of perfume in the same size range as the detergent and conditioning granules, as described in Example III.

Example VI

Liquid detergent compositions of the present invention are as follows:

Component	Weight %	
	A	B
C ₁₃ linear alkylbenzene sulfonic acid	7.2	7.2
C ₁₄₋₁₅ alkyl polyethoxylate (2.25) sulfuric acid	10.8	10.8
C ₁₂₋₁₃ alcohol polyethoxylate (6.5)*	6.5	6.5
C ₁₂ alkyl trimethylammonium chloride	1.2	0.6
C ₁₂₋₁₄ fatty acid	13.0	--
Oleic acid	2.0	--
Palm kernel fatty acid (stripped)	--	15.0
Citric acid (anhydrous)	4.0	4.0
Diethylenetriamine pentaacetic acid	0.23	0.23
Protease enzyme (2.0 AU/g)	0.75	0.75
Amylase enzyme (375 Am. U/g)	0.16	0.16
TEPA-E ₁₅₋₁₈ **	1.5	1.5
Monoethanolamine	2.0	--
(moles of alkanolamine)	(0.033)	(0)
Sodium ion	1.66	2.75
Potassium ion	2.65	2.55
(molar K + :Na +)	(0.94)	(0.55)
Propylene glycol	6.8	5.0
Ethanol	7.8	8.5
Formic acid	0.66	0.66
Calcium ion	0.03	0.03
Minors and water	Balance to 100	
pH at concentration of 10% in water at 68° F (20° C)	8.65	8.5

*Alcohol and monoethoxylated alcohol removed

**Tetraethylene pentamine ethoxylated with 15-18 moles (avg.) of ethylene oxide at each hydrogen site

Composition A is prepared by adding the components, with continuous mixing, in the following order: paste premix of alkylbenzene sulfonic acid, sodium hydroxide, propylene glycol and ethanol; paste premix of alkyl polyethoxylate sulfuric acid, sodium hydroxide and ethanol; pentaacetic acid; alcohol polyethoxylate; premix of water, brighteners, alkanolamine and alcohol polyethoxylate; ethanol; sodium and potassium hydroxide; fatty acid; citric acid; formic acid and calcium; alkyl trimethylammonium chloride; TEPA-E₁₅₋₁₈; adjust pH to about 8.1; and balance of components.

Composition B is prepared by adding the components, with continuous mixing, in the following order: paste premix of alkyl polyethoxylate sulfuric acid and ethanol; 2.5 parts water; propylene glycol; premix of ethanol and brightener; ethanol; premix of water, propylene glycol and brightener; alcohol polyethoxylate; sodium hydroxide; potassium hydroxide; fatty acid; alkylbenzene sulfonic acid; premix of citric acid and calcium; pentaacetic acid; formic acid; alkyl trimethylammonium chloride; TEPA-E₁₅₋₁₈; potassium hydrox-

ide and water; and balance of components.

Compositions A and B are isotropic liquids as made and remain isotropic down to about 50° F (10° C). They also recover to an isotropic form, after freezing and thawing, by about 55° F (12.8° C).

The above composition is combined with the perfume-containing particles of Example I as follows. An amount of the perfume particles of Example I is thoroughly mixed into the liquid detergent composition so that the detergent composition comprises about 0.3% perfume (about 1% of the detergent composition will comprise the perfume particles).

Example VII

An aqueous fabric softening composition containing as fabric softening active a 39.2:60.8 mixture of mono(hydrogenated tallow)trimethylammonium chloride and the reaction product of 2 moles of fatty acids with 1 mole of N-2-hydroxyethylethylenediamine is prepared as follows:

4.41 parts of reaction product of hydrogenated tallow fatty acids with N-2-hydroxyethylethylenediamine (Mazamide 6) are weighed into a premix vessel, followed by 5.68 parts of commercial mono(hydrogenated tallow)trimethylammonium chloride (Adogen 441, 50% active in 50% isopropanol). This premix is melted, mixed and heated to 77° C. The premix is then added, with agitation, to a mix vessel containing 89.87 parts of distilled water heated to 66° C, followed by 0.02 part of a commercial mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one (Kathon CG/ICP, 1.5% active, room temperature). The mixture is cooled to 49° C with continued agitation, and 0.02 part of a CaCl₂ solution (25% aqueous solution, room temperature) is added. At this stage the pH of the mixture is about 9.4. The pH is adjusted to 6.0 by the addition of a small amount of concentrated sulfuric acid.

The above composition is combined with the perfume-containing particles of Example I as follows. An amount of the perfume particles of Example I is combined with the fabric softening composition so that the composition comprises about 0.4% perfume (about 1-1/2% of the fabric softening composition will comprise the perfume particles).

Example VIII

A liquid fabric softening composition may be prepared as follows:

Component	% By Weight of Composition
1(2-Tallowyl Amidoethyl)-2 Tallowyl-imidazoline	4.85
DTDMAC	2.60
Silicone Oil (350 cst)	0.15
Hydrochloric Acid	0.30
Polyethylene Glycol	0.30
Bactericide	100 ppm
Water, Dye	Balance

The above composition is prepared using conventional means. The composition is combined with the perfume particles of Example II as follows. An amount of the perfume particles of Example II is combined with the fabric softening composition so that the composition comprises about 0.45% perfume (about 2% of the fabric softening composition will comprise the perfume particles).

The coated perfume particles provide enhanced protection against diffusion out of the perfume during product storage. When the composition is added to the laundry wash water (having a higher pH than the fabric softening composition), the coating material may be stripped away and the perfume is free to diffuse out of the particles more readily thereafter.

Another fabric softening composition may be made as above except that the levels of active components (i.e., everything but water and dye) are present at three times the levels quoted above. Yet another fabric softening composition may be made with the levels of active components being four times

those quoted above.

Example IX

A shampoo composition for the hair is prepared as follows:

Component	Weight %
Ammonium lauryl sulfate	12.0
Ammonium laureth (3) sulfate	4.0
Cetearyl alcohol	0.1
Glycol distearate	1.5
Cocamide MEA	1.0
Xanthan Gum	0.3
Dimethicone fluid viscosity 350 centistokes	1.8
Silicone gum (General Electric SE-76)	1.2
Lauryl trimethyl ammonium chloride	0.75
Color, preservative, pH control and water	q.s. 100%

The composition is made by preparing both a main mix and a premix. Into the main mix tank are put the ammonium lauryl sulfate and a part of the ammonium laureth sulfate. This mixture is heated to $120 \pm 10^\circ \text{F}$ with xanthan gum added next through a high shear pump. The total mixture is then heated to $155 \pm 5^\circ \text{F}$. Finally the glycol distearate, amide, part of the cetearyl alcohol and lauryl trimethyl ammonium chloride are added, followed by the color, perfume, preservative and part of the water.

The premix is prepared by adding the remainder of the ammonium laureth sulfate to the premix tank and heating to $155 \pm 5^\circ \text{F}$. The remainder of the cetearyl alcohol is then added and allowed to melt. Finally the dimethicone is added and mixed until an emulsion is formed.

The premix is mixed with the main mix through a static mixer, a higher shear mixer and finally through a heat exchanger. The total product is cooled to 80°F and collected.

The above composition is combined with the perfume-containing particles of Example II as follows. An amount of the perfume particles of Example II is combined with the shampoo composition so that the composition comprises about 0.2% perfume (about 1% of the shampoo composition will comprise the perfume particles).

Utilization of the perfume particles in the shampoo composition provides perfume fragrance in substantially its original state from product, through the hair washing process, to the hair.

Example X

A hair conditioning composition is prepared as follows:

Component	Weight %
C.S. 1213 silicone fluid ¹	0.83
Cetyl alcohol	1.00
Stearyl alcohol	0.72
Adogen 442 - 100P ²	0.85
Luviskol VA64 ³	0.25
Ceteareth-20 ⁴	0.35
Glycerol monostearate	0.25
Lexamine S-13 ⁵	0.50
Dow Corning 190 silicone surfactant ⁶	0.20
Hydroxyethyl cellulose	0.50
Citric acid	0.13
Preservative	0.03
Purified water	94.14

¹Mixture of 15% (by weight of mixture) SE76 dimethicone gum and 85% SF1201 cyclomethicone, sold by General Electric (providing a level of non-volatile silicone of 0.12%, by weight of composition)

²Di(hydrogenated tallow) dimethyl ammonium chloride, sold by Sherex Chemical Company, Inc.

³Copolymer of polyvinylpyrrolidone and vinyl acetate, sold by BASF A.G.

⁴Ethoxylated cetostearyl alcohol

⁵Stearamidopropyl dimethyl amine, sold by Inolex Corporation

⁶Dimethicone copolyol, sold by Dow Corning Corporation

The hydroxyethyl cellulose is added to the water, maintained at a temperature of approximately 38° C (100° F). The PVP/VA, Adogen, Dow-190, cetyl and stearyl alcohols, ceteareth-20, Lexamine and glycerol monostearate are then added sequentially at a temperature of approximately 87° C (189° F). The mixture is stirred after addition of each component for a period of time sufficient to allow proper melting of the component, i.e., the Adogen, and the dispersion into the product mixture.) The mixture is then cooled to approximately 48° C (118° F) at a rate of from about 1° to about 3° per minute. The citric acid, the dimethicone/cyclomethicone mixture, and preservative are then added. The mixture is then cooled and milled under high shear for approximately 1 minute using a conventional milling apparatus.

The above composition is combined with the perfume-containing particles of Example II as follows. An amount of the perfume particles of Example II is combined with the hair conditioning composition so that the composition comprises about 0.25% perfume (about 1% of the conditioner composition will comprise the perfume particles).

Approximately 10 g of the hair conditioning product thus formed is applied to freshly shampooed and rinsed hair. The composition is then spread over the hair and allowed to stand for approximately 1 minute. Thereafter, the product is rinsed from the hair, leaving the hair with enhanced fragrance benefits.

The following examples illustrate the preparation and use of perfume particles of the type of the present invention which additionally comprise a friable coating on the outside surface of the particles. Such coated particles are generally of a size less than 350 microns (including the coating) and preferably have an average size not greater than 150 microns, most preferably a size range of 40-150 microns.

Preferably, such particles are manufactured such that the friable coating comprises up to 20% by weight of the coated particles. Typically, the friable coating will comprise 1% to 10% by weight of the coated particles.

Various friable coatings can be used, but, preferably, the coating material is substantially water-insoluble. Typical friable coatings comprise aminoplast polymers, e.g., the reaction product of an amine and an aldehyde. Specific examples of such friable coatings include the reaction product of an amine selected from urea and melamine, and an aldehyde selected from formaldehyde, acetaldehyde and glutaraldehyde, and mixtures of said amines and said aldehydes.

Perfumed particles coated with friable coatings are especially useful in compositions which are agitated sufficiently that the coating ruptures to release the particle, which, in turn, releases its perfume. Cleaning compositions, conditioning compositions, and the like, especially those used in automatic machines, are nonlimiting examples of such compositions.

For particles with friable coatings, the process of manufacture is based on applying the coating as a kind of "shell" to the perfumed particles. For perfumed particles whose carrier material has a melting point below that of the boiling point of the solvent used in the process, the process involves melting the carrier and perfume together and adding the molten mixture to a solvent solution of the "shell" material, or a suitable precursor, held above the carrier melting temperature. The system is agitated sufficiently to form an emulsion of the carrier/perfume of desired liquid liquid drop size in the shell solution. The conditions necessary to deposit the encapsulating material are then established and the whole is cooled to give encapsulated solid particles having the desired, friable "shell". Water insolubility of the shell is established either at the deposition stage, or by suitable treatment prior to isolation or use of the particles.

Although the process described here is a one step molten drop formation/encapsulation procedure, it should be readily apparent to those skilled in the art that encapsulation of pre-formed perfume particles can be accomplished in a like manner. The pre-formed particles can be prepared in a variety of ways, including cryogrinding, spray drying, spray congealing and melttable dispersion techniques such as those described in books by P. B. Deasy ("Microencapsulation & Related Drug Processes", Dekker, N.Y., 1986) and A. Kondo ("Microcapsule Processing and Technology", Dekker, N.Y., 1979). Such techniques would be required for carrier materials having a melting point above the solvent boiling point.

A variety of suitable encapsulation procedures can be used, such as reviewed in the books by Deary and Kondo above. Depending on materials used, the shell can impart hydrophilicity or hydrophobicity to the particles. Nonlimiting examples of encapsulating materials and processes include gelatin-gum arabic concentrate deposited by a complex coacervation procedure, e.g., U.S. Patent 2,800,457, for hydrophilic shells, and ureaformaldehyde deposited by a polycondensation process, e.g., U.S. Patent 3,516,941, for hydrophobic shells.

Water insolubility of the shell materials may be imparted by cross-linking of the gelatin-gum arabic coacervate with suitable aldehydes or other known gelatin hardeners after deposition. Polymerization of the urea-formaldehyde precondensate during the encapsulation process yields water-insolubility.

The slurry containing the perfume particles can be used directly, e.g., spray dried with other components of the formulation, or the particles can be washed and separated, and dried if desired.

The following Examples further illustrate the manufacture of perfumed particles encapsulated with friable, preferably water-insoluble coatings and their use in typical detergent and softening compositions.

Example XI

Perfume particles containing a hydrophilic coating deposited by complex coacervation are prepared as follows.

132 g of POLYWAX 500 (polyethylene having a molecular weight of 500) is heated in a beaker on a hot plate at about 100° C until just melted. 44 g of perfume at room temperature is added to the melted POLYWAX 500 and heating is maintained to bring this core mixture back to 100° C.

The melted core material is added to 400 g of a 5% aqueous gelatin solution (Sanafi Type A, 275 Bloom strength) maintained 15-20° C above the core melting point in a 1-l steel beaker, and emulsified by agitation until desired drop size around 100 μ is reached. Then 200 g of hot, 11% gum arabic solution is added and agitation maintained for about 30 minutes.

The pH is reduced to around 4.2 by the dropwise addition of glacial acetic acid, and the beaker contents then poured into 1-l of stirred water at room temperature. This solidifies the core mixture with a concomitant deposition of gelatin-gum arabic coacervate.

The coating is set by chilling the slurry in ice water to around 5° C. The slurry may be used at this point, or the particle may be freed from any undeposited coacervate in the slurry by addition of about an equal volume of 10% sodium chloride and removing the capsules in a separatory funnel. This may be repeated as necessary to fully remove the free coacervate. The particles may be dried by filtering, washing the filter cake with water, then with inopropanol, followed by air drying overnight at 25° C.

The particles may then be sieved to desired size range.

Example XII

Perfume particles having a less water-soluble hydrophilic coating can be prepared as follows.

A slurry of perfume particles containing a gelatin-gum arabic coating are prepared as in Example 1. After chilling, the slurry is allowed to warm up to room temperature and 8.0 ml of 25% aqueous glutaraldehyde solution is added with stirring. The pH is raised to 5.0 by addition of 2.5% aqueous sodium hydroxide solution, and the slurry is stirred overnight.

5 The slurry may be used at this point, or separated as in Example 1.

The glutaraldehyde-treated coating can withstand prolonged immersion in water at 60°C, whereas untreated coatings are removed on heating to 50°C.

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Example XIII

Perfume particles containing a hydrophobic, water-insoluble coating deposited by polycondensation are prepared as follows.

15 A urea-formaldehyde precondensate is first formed by heating a mixture of 162 g 37% aqueous formaldehyde and 60-65 g urea, adjusted to pH 8.0 with 0.53 g sodium tetraborate, for 1 hour at 70°C, and then adding 276.85 g water.

429 ml of this precondensate and 142 ml water are then stirred in a 1-l steel reactor and 57.14 g sodium chloride and 0.57 g sodium carboxymethyl cellulose added. Then are added the core components comprising 161.3 g POLYWAX 500 carrier and 60.7 ml perfume, and the reactor is heated to about 10°C 20 above the core melting point. Agitation is adjusted to emulsify and maintain the molten core at the desired drop size, and the pH of the contents is adjusted to about 5.0 with dilute hydrochloric acid.

The reactor is then allowed to cool to room temperature with a gradual pH reduction to 2.2 over a 2 hour period. The reactor is then increased to about 50°C for a further 2 hours, then cooled to room 25 temperature, after which the pH is adjusted to 7.0 with 10% sodium hydroxide solution.

The resultant slurry containing the solid core particles encapsulated with urea-formaldehyde polymer may be used directly, or may be isolated by separation, washing and air drying as required.

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Example XIV

A granular laundry detergent comprises the detergent composition of Example IV(A), above, but with replacement of the perfumed particles of that example with an equivalent amount (2% by weight of finished 35 composition) of the particles with the friable urea-formaldehyde coating, made according to Example XI, and comprising about 10% (by weight of perfumed particle) of said coating (average size of coated particle <150 microns).

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Example XV

The detergent of Example XIV is duplicated, using the friable coating of Examples XII and XIII, respectively, at a coating weight of about 1%-5% (avg.) by weight of perfumed particle (avg. coated particle 45 size in the range 40-150 microns).

Example XVI

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A liquid laundry detergent is prepared according to Example VI(A), but with replacement of the perfumed particles of that example with 3% by weight of the coated perfumed particles of Example XII (avg. coating wt. 5%-7%; avg. coated particle size in the range 40-100 microns).

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Example XVII

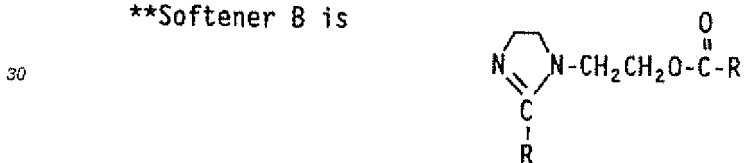
A fabric softener for use in an aqueous laundry rinse bath is as follows.

	<u>Component</u>	<u>Weight %</u>
5	Softener A*	3.00
	Softener B**	5.00
	HCl	0.29
10	Polydimethylsiloxane	0.15
	Polyethylene Glycol (4000)	0.30
	Bronopol (Antimicrobial)	100 ppm
	Calcium Chloride	30 ppm
15	Dye	30 ppm
	Coated Perfume Particles***	4.0
	Water	Balance

20 *Softener A is
$$\text{RCOCH}_2\text{CH}_2\text{N}^+\text{R}(\text{CH}_3)_2, \text{Cl}^-$$
 wherein each R group is in the C₁₅-C₁₈ alkyl range.

25

**Softener B is



wherein each R group is in the C₁₅-C₁₈ alkyl range.

35 ***Particles prepared according to Example XII. 100 micron size;
5% coating weight.

40 When used in the rinse bath of an automatic washing machine, the coating on perfumed particles of Example XVII is ruptured and the particles provide a fragrance to the fabrics being treated.

45 Example XVIII

A fabric softener for use in an aqueous laundry rinse bath is as follows.

50

55

Component	Weight %
Softener C ⁺	3.7
TAMET ^{**}	0.3
GMS ^{***}	1.20
Phosphoric Acid	0.023
Polydimethylsiloxane (350)	0.10
Glutaraldehyde	550 ppm
Blue Dye	10 ppm
Coated Perfume Particles ^{****}	3.0

⁺(R¹)₂(CH₃)₂N⁺, Br⁻, wherein R¹ is mixed C₁₂-C₁₈ alkyl (i.e., "tallowalkyl").

^{**}TAMET is tallowalkyl N (CH₂CH₂OH)₂.

^{***}GMS is glyceryl monostearate.

^{****}Coated perfume particles per Example XIII, sieved to average size less than 150 microns. Coating weight 3%.

It will be appreciated by those skilled in the art that the anions, X, used with any of the cationic fabric softeners herein are a routine matter of choice, and that X can be, for example, chloride, bromide, methylsulfate, and the like. Mixtures of fabric softeners can be used, as can mixtures of anions.

Example XIX

The detergent composition of Example VI(A) is modified by using perfumed particles with friable coatings (melamine/urea/formaldehyde; 0.1/1/1.1 mole ratio; 300 micron size) with coating weights of 1% and 20%, respectively.

It will be appreciated by the formulator that the weight (or thickness) of operable friable coatings can be adjusted according to the usage envisioned. For example, even relatively thick coatings will rupture and release their perfume particles under European machine washing conditions, which can involve wash times of many minutes, at high temperature and considerable agitation. By contrast, USA machine washing conditions are much shorter, and milder, so less coating material should be used. For fabric softeners, agitation and agitation times are usually less than for washing.

Claims

1. Perfume particles having an average size of less than 350 microns, preferably less than 300 microns which comprise from 5% to 70%, preferably 5% to 50%, by weight of a perfume, characterized in that said perfume is dispersed in from 30% to 95% of a water-insoluble polymeric carrier material having a molecular weight of from 100 to 30,000, a melting point of from 37° C to 190° C, and a hardness value of from 0.1 to 15.
2. The particles of Claim 1 wherein the carrier material has a molecular weight of from 500 to 5,000, and a hardness value of from 0.1 to 8.
3. The particles of Claim 2 wherein the carrier material is selected from the group consisting of polyethylenes, polyamides, polystyrenes, polyisoprenes, polycarbonates, polyesters, polyacrylates, vinyl polymers, polyurethanes, and mixtures thereof.
4. The particles of Claim 3 wherein the carrier material comprises polyethylene.
5. The particles of Claim 1 additionally comprising from 5% to 50% of a pH-sensitive material coating the outside surface of the particle.
6. The particles of Claim 5 wherein the pH-sensitive material is selected from the group consisting of acrylic resins, cellulose acetate phthalate and cellulose acetate trimellitate.
7. The particles of Claim 6 wherein the pH-sensitive material additionally comprises from 0.5% to 10%, by weight of the perfume particles, of a plasticizer material selected from the group consisting of diethyl phthalate, tributyl citrate, and acetyltributyl citrate.

8. The particles of Claim 1 additionally comprising from 1% to 25% of a fabric substantive material coating the outside surface of the particle, wherein said fabric substantive material is selected from the group consisting of ditallowalkyldimethylammonium methylsulfate, ditallowalkyldimethylammonium chloride, dicoconutalkyldimethylammonium methylsulfate, dicoconutalkyldimethylammonium chloride, and mixtures thereof.

9. A detergent composition comprising:

(a) from 1% to 90% of a surfactant selected from the group consisting of anionic, nonionic, zwitterionic, cationic, ampholytic surfactants, and mixtures thereof; and

(b) an amount of the perfume particles of Claim 1 to provide the composition with from 0.001% to 10% of perfume.

10. A detergent composition according to Claim 9 comprising:

(a) from 10% to 40% of a surfactant selected from the group consisting of anionic, nonionic, zwitterionic, ampholytic, cationic surfactants, and mixtures thereof;

(b) from 5% to 50% of a detergency builder material; characterized in that it contains

(c) an amount of the perfume particles of Claim 6 to provide the composition with from 0.1% to 3.0% perfume.

11. A fabric conditioning composition comprising:

(a) from 1% to 90% of a conditioning agent selected from the group consisting of cationic softeners; characterized in that it contains

(b) an amount of the perfume particles of Claim 1 to provide the composition with from 0.001% to 10% of perfume.

12. A conditioning composition according to Claim 11 comprising:

(a) from 3% to 35% of a cationic softener selected from the group consisting of mononitrogen quaternary ammonium cationic salts, imidazolinium salts, di(2-amidoethyl)methyl quaternary ammonium salts, 1(2-tallowylamidoethyl)-2 tallowylimidazoline, and mixtures thereof; and

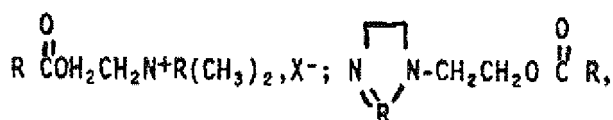
(b) an amount of the perfume particles of Claim 6 to provide the composition with from 0.1% to 3.0% perfume.

13. A laundry bleach composition comprising:

(a) from 2% to 50% of a bleaching agent; characterized in that it contains

(b) an amount of the perfume particles of Claim 1 to provide the composition with from 0.1% to 10% perfume.

14. A softener composition comprising a fabric- or fiber-softening or antistatic agent selected from



wherein each R is in the C₁₅-C₁₈ alkyl range; and (R')₂(CH₃)₂N⁺X⁻, wherein each R' group is C₁₂-C₁₈ alkyl; and mixtures thereof; and wherein X is an anion, characterized in that it contains the perfumed particles of Claim 1 encapsulated by a friable coating.

(19)



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(54) **Detergent composition**

(57) A laundry additive composition comprising one or more perfume components in slow release form and wherein the release kinetics are controlled so as to provide a fabric delivery index of at least 0.3.

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Description**Field of the invention**

5 [0001] The present invention relates to solid compositions comprising a perfume, especially solid laundry detergent compositions comprising a perfume.

Background to the invention

10 [0002] Laundry detergent products typically comprise a perfume. The function of this perfume is to mask the undesirable odour of the detergent components in the product and to ensure that the detergent has a desirable smell that consumers find appealing throughout the duration of a laundering process; this includes during dispensing of the product (neat product odour), and during the washing and drying stages (wet fabric odour) of the laundering process. In addition, it is also desirable for the perfume to give the recently laundered dry fabric a pleasant odour (dry fabric odour).

15 [0003] Perfumers attempt to meet the demanding consumer need of having a laundry detergent product that delivers good neat product odour, good wet fabric odour and good dry fabric odour performance, by formulating perfumes that comprise several perfume components that are designed to deliver a specific odour at a specific stage in the laundering process. However, it is difficult to formulate a perfume that is capable of adequately delivering the desired odour during the desired stage in the laundering process, and which does not affect the performance of the other perfume components in the perfume. This is due to the unwanted early release (i.e. leakage) of fragrance from perfume components, which affects the performance of other perfume components that are designed to deliver a perfume odour during earlier stages of the laundering process.

20 [0004] Perfumers have attempted to overcome this problem by designing a perfume containing composition, which comprises perfume components that are compatible with each other and deliver fragrances that are compatible with the fragrances that are delivered by the other perfume components, in order to negate the effect that any leakage of one perfume component fragrance may have on another perfume component fragrance. However, in order to achieve this fragrance compatibility, perfumers have had to formulate very complex and costly perfumes having very limited choice in which perfume raw materials they can choose when formulating a perfume containing composition or component thereof.

Summary of the invention

25 [0005] The present invention overcomes this problem by providing a laundry additive composition comprising one or more perfume components in slow release form and wherein the release kinetics are controlled so as to provide a fabric delivery index of at least 0.3. The fabric delivery

$$\text{index} = \frac{\text{the concentration of perfume component in the headspace of dry fabric}}{\text{the concentration of perfume component in the headspace of wet fabric}}$$

40 [0006] A further embodiment of the present invention provides a laundry detergent composition comprising the above laundry additive composition.

45 [0007] A further embodiment of the present invention provides a process for preparing a perfume particle, the process comprises the steps of: (a) contacting a perfume with a porous carrier material, to form a perfume-loaded material; and (b) contacting the perfume-loaded material with an aqueous solution or dispersion of encapsulating material, to form an intermediate mixture; and (c) drying the intermediate mixture to form a perfume particle; wherein, the perfume-loaded material is in contact with the aqueous mixture of encapsulating material for a period of time of less than 120 minutes, prior to drying.

Detailed description of the invention**Perfume component**

50 [0008] The perfume component typically comprises one or more perfume raw materials (PRMs), more typically the perfume component comprises at least two, or at least five or even at least 10 or more PRMs, which are typically blended together to obtain a perfume accord that has a particular desired odour. The perfume component comprises all of the PRMs that share the same method of incorporation. For example, all of the PRMs that are delivered by a spray-on delivery system form one perfume component (e.g. form a spray-on perfume component). The perfume component is typically a selection of PRMs that are blended together to obtain a particular perfume accord such as a fruity

perfume accord. Typical PRMs suitable for use are selected from the group consisting of aldehydes, ketones, esters, alcohols, propionates, salicylates, ethers and combinations thereof. Typically, the PRMs are liquid, especially at ambient temperature and pressure. Usually, the PRMs are synthetic molecules. Alternatively, the PRMs can be derived from animals or plants. The perfume component can be formulated to provide any olfactory perception that is desired. For example, the perfume component can be a light floral fragrance a fruity fragrance or a woody or earthy fragrance. The perfume component may be of a simple design and comprise only a relatively small number of PRMs, or alternatively the perfume component may be of a more complex design and comprise a relatively large number of PRMs. Preferred perfume components and PRMs are described in more detail in WO97/11151, especially from page 8, line 18 to page 11, line 25, which is herein incorporated by reference.

[0009] The perfume component typically has a threshold olfactory detection level, otherwise known as an odour detection threshold (ODT) of less than or equal to 3ppm, more preferably equal to or less than 10ppb. Typically, the perfume component comprises PRMs that have an ODT of less than or equal to 3ppm, more, preferably equal to or less than 10ppb. Preferred is when at least 70wt%, more preferably at least 85wt%, of the PRMs that are comprised by the perfume component have an ODT of less than or equal to 3ppm, more preferably equal to or less than 10ppb. A method of calculating ODT is described in WO97/11151, especially from page 12, line 10 to page 13, line 4, which is herein incorporated by reference.

[0010] Typically, the perfume component has a boiling point of less than 300°C. Typically, the perfume component comprises at least 50wt%, more preferably at least 75wt%, of PRMs that have a boiling point of less than 300°C. In addition, the perfume component has an octanol/water partition coefficient (ClogP) value greater than 1.0. A method of calculating ClogP is described in WO97/11151, especially from page 11, line 27 to page 12, line 8, which is herein incorporated by reference.

[0011] The perfume component can be contained in a particle, and is typically adsorbed or absorbed onto a porous carrier material. The porous carrier and adsorption/absorption process is described in more detail below. Perfume components that are adsorbed/absorbed onto porous carriers can be tailored in such a way to delay the release of the perfume component from the porous carrier.

[0012] One means of tailoring a perfume component to be released slowly from a porous carrier material is to ensure that the perfume component comprises one or more perfume raw materials that have good affinity for the porous carrier material. For example, PRMs that have a specific size, shape (i.e. a molecular cross-sectional area and molecular volume), and surface area relative to the pores of the porous carrier material exhibit improved affinity for the porous carrier material, and are able to prevent other PRMs that have less affinity to the porous carrier material, from leaving the porous carrier material during the washing and rinsing stage of the laundering process. This is described in more detail in WO97/11152, especially from page 7, line 26 to page 8, line 17, which is herein incorporated by reference.

[0013] Other means of tailoring a perfume component to be released slowly from a porous carrier material is to ensure that the perfume component comprises PRMs that are small enough to pass through the pores of the carrier material, and that are capable of reacting together, or with a small non-perfume molecule (otherwise known as a size-enlarging agent) to form a larger molecule (other wise known as a release inhibitor) that is too large to pass through the pores of the carrier. The release inhibitor, being too large to pass through the pores of the porous carrier material, becomes entrapped within the porous carrier material until it breaks down (i.e. hydrolyses) back to the smaller PRM and size enlarging agent, which are then able to pass through the pores of, and exit, the porous carrier material. Typically, this is achieved by the formation of hydrolysable bonds between small PRMs and the size-enlarging agent, to form a release inhibitor within the porous carrier material. Upon hydrolysis, the small PRMs are released from the larger molecule and are able to exit the porous carrier material. This is described in more detail in WO97/34981, especially from page 7, line 4 to page 5, line 14, which is herein incorporated by reference.

[0014] In addition, the above approach of forming a release inhibitor by reacting a PRM with a size-enlarging agent can be further adapted by using a size enlarging agent that has a hydrophilic portion and a hydrophobic portion (e.g. sugar based non-ionic surfactants, such as lactic acid esters of C₁₈ monoglycerides). This is described in more detail in WO97/34982, especially from page 6, line 27 to page 7, line 17, which is herein incorporated by reference.

[0015] The perfume component can be a starch encapsulated perfume accord or another type of perfume component having controlled release kinetics. And one or more perfume components can be present in the composition. However, it is essential that at least one perfume components is in slow release form and the release kinetics are controlled so as to provide a fabric delivery index of at least 0.3, preferably at least 0.5 or even at least 0.7.

Perfume particle

[0016] Typically, the perfume component is contained in a perfume particle. The perfume particle is used to give a dry fabric odour benefit to a fabric. The perfume particle comprises a perfume component in slow release form, wherein the release kinetics are controlled so as to provide a fabric delivery index of at least 0.3, preferably at least 0.5 or at least 0.7 and may even be from 0.7 to 1.0. The perfume particle may also comprise a porous carrier material. The

porous carrier material is described in more detail below. The perfume component in the perfume particle is typically at least partially encapsulated, preferably completely encapsulated with an encapsulating material. The encapsulating material is described in more detail below. Typically, the perfume component is absorbed and/or adsorbed onto the porous carrier to form a perfume-loaded material, and the perfume-loaded material is then at least partially encapsulated, preferably completely encapsulated with the encapsulating material to form a perfume particle. The process of preparing the perfume particle is described in more detail below.

[0017] The perfume particle may be coated. Preferred coating means are described in WO98/12291 and WO98/42818, which are herein incorporated by reference.

[0018] Typically, the perfume particle is a glassy particle and preferably has a hygroscopicity value of less than 80%. The hygroscopicity value is the level of moisture uptake by the perfume particle, as measured by a weight percent increase in the weight of the perfume particle. The hygroscopicity value and a method for measuring it are described in more detail in WO97/11151, especially from page 7, line 11 to page 7, line 20, which is incorporated herein by reference.

[0019] The perfume particle typically comprises from 3% to 50% preferably from 5% to 20%, by weight of the perfume particle, of perfume component. The perfume particle may comprise from 15% to 80%, preferably from 20% to 65%, by weight of the perfume particle, of encapsulating material. The perfume particle may comprise other adjunct components, although preferably the perfume particle comprises essentially only of perfume component, porous carrier, encapsulating material and water.

Porous carrier material

[0020] The porous carrier material can be any porous material that is capable of supporting (e.g. by absorption or adsorption) the perfume component. Typically, the porous carrier material is substantially water-insoluble. Preferred porous carrier materials are selected from the group consisting of amorphous silicates, crystalline non-layered silicates, calcium carbonates, calcium/sodium carbonate double salts, sodium carbonates, clays, aluminosilicates, chitin micro beads, cyclodextrins, and combinations thereof. More preferably, the porous carrier material is an aluminosilicate, most preferably a zeolite, especially a faujasite zeolite, such as zeolite X, zeolite Y and combinations thereof. An especially preferred porous carrier is zeolite 13x. Preferred aluminosilicates are described in more detail in WO97/11151, especially from page 13, line 26 to page 15, line 2, which is herein incorporated by reference.

[0021] It may be preferred for the porous carrier to have a crystalline structure and to have a primary crystal size of 20 microns or bigger. Larger primary particle sized porous carriers are more likely to become entrapped onto fabric during the washing stage of the laundering process, and thus show improved fabric deposition. Porous carriers having a primary crystal size of 20 microns or greater, show improved dry fabric odour performance, believed to be due to improved fabric deposition. However, porous carrier materials having a smaller primary crystal size, e.g. from 0.01 to 7 microns or even to 5 microns, are more readily commercially available and can be used in accordance with the present invention. The larger primary crystal sizes are especially preferred when the porous carrier is an aluminosilicate, especially a zeolite X and/or Y.

Encapsulating material

[0022] The encapsulating material typically encapsulates at least part, preferably all, of the perfume component and, if present, the porous carrier material. Typically, the encapsulating material is water-soluble and/or water-dispersible. The encapsulating material may have a glass transition temperature (T_g) of 0°C or higher. Glass transition temperature is described in more detail in WO97/11151, especially from page 6, line 25 to page 7, line 2, which is incorporated herein by reference.

[0023] The encapsulating material is preferably selected from the group consisting of carbohydrates, natural or synthetic gums, chitin and chitosan, cellulose and cellulose derivatives, silicates, phosphates, borates, polyvinyl alcohol, polyethylene glycol, and combinations thereof. Preferably the encapsulating material is a carbohydrate, typically selected from the group consisting of monosaccharides, oligosaccharides, polysaccharides, and combinations thereof. Most preferably, the encapsulating material is a starch. Preferred starches are described in EP 0 922 499, US 4 977 252, US 5 354 559 and US 5 935 826.

Fabric delivery index

[0024] The fabric delivery index is a measure of how much of the perfume component is released from the dry fabric and how much is released from the wet fabric. The fabric delivery index is a ratio of the concentration of perfume component in the headspace of dry fabric: concentration of perfume component in the headspace of wet fabric, and is represented by the following:

the concentration of perfume component in the headspace of dry fabric
the concentration of perfume component in the headspace of wet fabric.

At least one perfume component is in slow release form, wherein the release kinetics are controlled so as to provide a fabric delivery index of at least 0.3, preferably at least 0.5 and most preferably at least 0.7. It may be preferred that the fabric delivery index is from 0.7 to 1.0.

[0025] Typically, the concentration of perfume component in the headspace of dry fabric is determined by the following method: The perfume component is added to detergent adjunct components to make the following solid granular composition: 0.1wt% perfume component, 7.5wt% sodium linear C₁₁₋₁₃ alkyl benzene sulphonate, 3.5wt% linear C₁₂₋₁₄ linear primary alcohol condensed with an average of 7 moles of ethylene oxide per mole of alcohol, 1wt% cationic surfactant of the formula: RN⁺(CH₃)₂(C₂H₄OH) wherein R = C₁₂₋₁₄ linear alkyl chain, 20% anhydrous sodium tripolyphosphate, 20wt% sodium carbonate, 3wt% sodium silicate, 6wt% moisture, to 38.9wt% sodium sulphate. At least 121.5g of the solid granular composition is left in storage for 14 days at ambient temperature, pressure and relative humidity in closed glass container.

[0026] After 14 days storage, 24 10cm square terry towel cloths are placed in an automatic washing machine (Miele Novotronic W918) along with an equal weight of terry towel material to act as the ballast during the laundering process. 121.5g of the solid granular composition is added to the dispensing draw of the automatic washing machine, and the terry towel cloths undergo a washing programme at 40°C (40°C, short wash, minimum iron, 1,000rpm spin) with a main wash cycle of 20 minutes and 4 rinse cycles lasting a total of 20 minutes.

[0027] After the washing stage, 12 of the terry towel cloths (wet terry towel cloth) are then analysed and the concentration of the perfume component in the headspace of the wet fabric is determined. This is described in more detail below. The remaining 12 terry towel cloths are dried using an automatic drier (Miele Dryer Machine Novotronic T640) for a first drying stage of 40 minutes at normal temperature settings (80°C) and a second drying stage of 20 minutes at warm (50°C) temperature settings. The 12 terry towel cloths are left to cool for one hour (dry terry towel cloths) and are then analysed and the concentration of the perfume component in the headspace of the dry fabric is determined. This is described in more detail below.

[0028] The concentration of the perfume component in the headspace of the wet and dry fabric, respectively, is determined by the following method. The terry towel cloth is placed in a sealed glass container containing a polydimethyl siloxane (PDMS) Twister Gerstel™ Bar of 0.5mm thickness and 20mm length. The bar, which is never in direct physical contact with the fabric, is exposed to wet terry towel cloths for 3 hours and to dry terry cloths for 15 hours, respectively. The bar is then transferred to an autodesorb glass lined stainless steel tube (GLT) of a Gas Chromatography Agilent 6890™ with MS detector 5973™. The GLT is placed in the autodesorb carousel for injection. Gas chromatography is then carried out and the concentration of the perfume component (in the headspace of the fabric) is determined.

Composition

[0029] The laundry additive composition is typically a solid composition, preferably a solid particulate composition. The composition is used to give a dry fabric odour benefit to a fabric. It is a laundry additive or auxiliary composition and can be used separately from any other fabric treatment composition or, alternatively, can be contained in a laundry detergent composition. Typically, the laundry additive composition is contained in a laundry detergent composition. The laundry additive composition, and more preferably the laundry detergent composition may optionally comprise adjunct components, typically laundry detergent adjunct components. These adjunct components are described in more detail below. The composition may be the product of a spray-dry and/or agglomeration process. A preferred process for preparing the perfume component is described in more detail below.

[0030] The laundry additive composition comprises one or more perfume components in slow release form. The perfume component is described in more detail above. The composition comprises at least one perfume component in slow release form, wherein the release kinetics are that has a fabric delivery index of at least 0.3, preferably at least 0.5, or even at least 0.7. The perfume component may have a fabric delivery index of from 0.7 to 1.0.

[0031] The laundry additive composition may also additionally comprise at least one perfume component of a different composition and olfactory character having a fabric delivery index for dry versus wet fabrics of less than 0.1, preferably less 0.05, more preferably less than 0.01. This further allows the delivery of different olfactory characters to wet and dry fabric, respectively, and negates the need to ensure that the two different perfume components have compatible fragrances.

[0032] The composition comprises from 0% to 26%, by weight of the composition, of phosphate. Preferably, the composition comprises 0%, by weight of the composition, of phosphate. Typically, the composition is free from deliberately added phosphate.

Adjunct components

[0033] The composition may optionally comprise adjunct components, preferably laundry detergent adjunct components. These adjunct components are typically selected from the group consisting of deterative surfactants, builders, polymeric co-builders, bleach, chelants, enzymes, anti-redeposition polymers, soil release polymers, polymeric soil dispersing and/or suspending agents, dye transfer inhibitors, fabric integrity agents, brighteners, suds suppressors, fabric softeners, flocculants, and combinations thereof. Suitable adjunct components are described in more detail in WO97/11151, especially from page 15, line 31 to page 50, line 4, which is incorporated herein by reference.

Process for preparing the perfume particle

[0034] The perfume particle is obtained by a process comprising the steps of: (a) contacting a perfume component with a porous carrier material, to form a perfume-loaded material; and (b) contacting the perfume-loaded material with an aqueous solution or dispersion of encapsulating material, to form an intermediate mixture; and (c) drying the intermediate mixture to form a perfume particle. The perfume-loaded material is in contact with the aqueous mixture of encapsulating material for a period of time of less than 120 minutes, preferably less than 90 minutes, even more preferably less than 60 minutes, and most preferably less than 30 minutes or even less than 20 minutes, prior to drying. It may even be preferred that the perfume-loaded material is in contact with the aqueous mixture of encapsulating material for a period of time of from 0.001 minutes to 20 minutes, or even from 10 minutes to 20 minutes, prior to drying. The less time that the perfume loaded material is in contact with the aqueous mixture of encapsulating material, then the less leakage of PRMs from the porous carrier material occurs. This results in the formation of perfume particle that has a higher fabric delivery index and gives an improved fabric odour benefit during the laundering process. However, this period of time still needs to be long enough to ensure that adequate encapsulation of the perfume component and porous carrier occurs.

[0035] The first step, step (a), of contacting a perfume component to with a porous carrier material to form a perfume-loaded material can occur in any suitable mixing vessel. Typically, step (a) is carried out in an Schugi, or other high shear mixer, for example a CB mixer, although other lower shear mixers, such as a KM mixer, may also be used. Typically, the porous carrier material is passed through the high shear mixer and the perfume component is sprayed onto the porous carrier material. The adsorption of perfume component onto the porous carrier material is typically an exothermic reaction and heat may be generated during this stage of the process (depending on the PRMs and porous carrier material used). When the porous carrier material is an aluminosilicate such as zeolite 13x, then a substantial amount of heat can be generated during step (a). The generation of heat can be controlled by any suitable heat management means; such as placing water jackets or coils on the mixer or other vessel used in step (a), or by direct cooling, for example by using liquid nitrogen, to remove the heat that is generated, and/or by controlling the flow rate of the porous carrier material and perfume component in the mixer or other vessel used in step (a) to prevent the build up of an excess amount of heat during step (a). The build up of heat during step (a) is more likely to occur and be a problem when the process is a continuous process.

[0036] The second step, step (b), of contacting the perfume-loaded material with an aqueous solution or dispersion of encapsulating material to form an intermediate mixture, can occur in any suitable vessel such as a stirred tank. Alternatively, step (b) can occur in an online mixer. The stirring tank can be a batch tank or a continuous tank. As described above, the time that the perfume-loaded material is in contact with the aqueous mixture of encapsulating material needs to be carefully controlled in order to obtain a perfume particle that gives a good dry fabric odour benefit.

[0037] It is also preferred to control the temperature of step (b) in order to obtain perfume particles having a good dry fabric odour performance. Preferably, step (b) is carried out at a temperature of less than 50°C, or even less than 20°C. It may be preferred that cooling means such as a water jacket or even liquid nitrogen are used in step (b), this is especially preferred when it is desirable to carry out step (b) at a temperature that is below the ambient temperature.

[0038] It may also be preferred to limit the energy condition of step (b) in order to obtain a perfume particle that has a good dry fabric odour performance. Step (b) is preferably done in a low shear mixer, for example a stirred tank.

[0039] The third step, step (c), of drying the intermediate mixture to form a perfume particle can be carried out in any suitable drying equipment such a spray-dryer and/or fluid bed dryer. Typically, the intermediate mixture is forced dried (for example, spray-dried or fluid bed dried) and is not simply left to dry by evaporation at ambient conditions. Typically, heat is applied during this drying step. Typically, the intermediate mixture is spray-dried. Preferably, the temperature of the drying step is carefully controlled to prevent the perfume component from vapourising and escaping from the perfume particle, which reduces the perfume particles dry-fabric odour performance. Preferably, the intermediate mixture is spray-dried in a spray-drying tower, and preferably the difference between the inlet air temperature and the outlet air temperature in the spray-drying tower is less than 100°C. This is a smaller temperature difference than is conventionally used in spray-drying laundry detergent components but (as explained above) is preferred in order to prevent the unwanted vapourisation of the volatile PRMs from the perfume component. Typically, the inlet air temper-

ature of the spray-drying tower is from 170°C to 220°C, and the outlet air temperature of the spray-drying tower is from 80°C to 110°C. Highly preferred is when the inlet air temperature of the spray-drying tower is from 170°C to 180°C, and the outlet air temperature of the spray-drying tower is from 100°C to 105°C. It is also important that a good degree of atomisation of the intermediate material is achieved during the spray-drying process, as this ensures that the perfume particles have the optimal particle size distribution, having good flowability, solubility, stability and dry fabric odour performance. The degree of atomisation can be controlled by carefully controlling the tip speed of the rotary atomiser in the spray-drying tower. Preferably, the rotary atomiser has a tip speed of from 100ms⁻¹ to 500ms⁻¹.

[0040] It may be preferred that during its processing and storage thereafter, the perfume particle and any intermediate product that is formed during its processing, is kept in an environment having a low relative humidity. Preferably the air immediately surrounding the perfume particle (or intermediate material thereof) is the equal to or lower than, preferably lower than, the equilibrium relative humidity of the perfume particle (or intermediate material thereof). This can be achieved, for example, by placing the perfume particle in air tight containers during storage and/or transport, or by the input of dry and/or conditioned air into the mixing vessels, storage and/or transport containers during the process, transport and/or storage of the perfume particle (or intermediate material thereof).

[0041] Perfume particles that are obtained by the above process have a high fabric delivery index and good dry fabric odour performance.

Examples

Example 1

[0042] The following perfume accords are suitable for use in the present invention. Amounts given below are by weight of the perfume accord.

Perfume accord A		
PRM trade name	PRM chemical name	Amount
Damascone beta TM	2-buten-1-one, 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-	1%
Dynascone 10 TM	4-Penten-1-one, 1-(5,5-dimethyl-1-cyclohexen-1-yl)-	5%
	Ethyl 2 Methyl Butyrate	6%
Eugenol	4-hydroxy-3-methoxy-1-allylbenzene	1%
Cyclacet TM	Tricyclo decenyl acetate	3%
Cyclaprop TM	Tricyclo decenyl propionate	6%
ionone beta TM	2-(2,6,6-Trimethyl-1-cyclohexen-1-yl) -3-buten-2-one	8%
Nectaryl TM	2-(2-(4-Methyl-3-cyclohexen-1-yl)propyl) cyclopentanone	50%
Triplal TM	3-cyclohexene-1-carboxaldehyde, dimethyl	10%
Verdox TM	Ortho tertiary butyl cyclohexanyl acetate	10%

[0043] Perfume accord A is an example of a fruity perfume accord.

Perfume accord B		
PRM trade name	PRM chemical name	Amount
Ally amyl glycolate TM	Glycolic acid, 2 -pentyloxy:allyl ester	5%
Damascone beta TM	2-buten-1-one, 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-	2%
Dynascone 10 TM	4-Penten-1-one, 1-(5,5-dimethyl-1-cyclohexen-1-yl)-	5%
Hedione TM	Cyclopentaneacetic acid, 3-oxo-2-pentyl- methyl ester	25%
Iso cyclo citral	3-cyclohexene-1-carboxaldehyde, 2,4,6-trimethyl	5%
Lilial TM	2-Methyl-3-(4-tert-butylphenyl)propanal	48%
Rose oxide	Methyl iso butenyl tetrahydro pyran	5%

(continued)

Perfume accord B		
PRM trade name	PRM chemical name	Amount
Triplal™	3-cyclohexene-1-carboxaldehyde, dimethyl	5%

[0044] Perfume accord B is an example of a floral green perfume accord.

Perfume accord C		
PRM trade name	PRM chemical name	Amount
Hedione™	Cyclopentaneacetic acid, 3-oxo-2-pentyl- methyl ester	30%
Isoraldeine 70™	Gamma-methylionone	30%
Dodecanal	Lauric Aldehyde	1%
Lilial™	2-Methyl-3-(4-tert-butylphenyl)propanal	30%
	Methyl Nonyl Acetaldehyde	1%
Triplal™	3-cyclohexene-1-carboxaldehyde, dimethyl	5%
	Undecylenic Aldehyde	3%

[0045] Perfume accord C is an example of a floral aldehydic perfume accord.

Example 2

[0046] The perfume accords of example 1 undergo the following process to obtain perfume particles that are suitable for use in the present invention.

[0047] Zeolite 13x is passed through a Schugi mixer, wherein the perfume accord is sprayed onto the zeolite 13x to obtain perfume-loaded zeolite 13x comprising 85% zeolite 13x and 15% perfume accord. The Schugi mixer is operated at 2,000rpm to 4,000 rpm. Liquid nitrogen is used to control the build up of heat that occurs during this perfume-loading step, which is carried out at a temperature of below 40°C.

[0048] Water and starch are mixed together to form an aqueous mixture of starch. The perfume-loaded zeolite 13x is added to this aqueous mixture of starch to form an encapsulation mixture comprising 10.5wt% starch, 24.5wt% perfume-loaded zeolite 13x, and 65wt% water. This is carried out in a batch container. The time of this step is less than 20 minutes.

[0049] The encapsulation mixture is fed continuously to a buffer tank, from where it is spray dried. The encapsulation mixture is pumped into a Production Minor using a peristaltic pump and then spray dried to obtain perfume particles. The rotary atomiser tip speed was 151.8 m/s (29000 rpm of a 10 cm diameter atomiser). The inlet temperature of the spray-drying tower is 170°C and the outlet temperature of the spray-drying tower is 105°C.

[0050] The particles obtained by this process comprise a perfume component in slow release form and wherein the release kinetics are controlled so as to provide a fabric delivery index for dry versus wet fabrics of at least 0.3.

Example 3

[0051] The perfume particles of example 2 are incorporated into the following solid laundry detergent composition, which are suitable for use in the present invention. Amounts given below are by weight of the composition.

Ingredient	A	B	C	D	E	F
Sodium linear C ₁₁₋₁₃ alkylbenzene sulphate	15%	18%	15%	11%	10%	8%
R ₂ N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH), wherein R ₂ =C ₁₂ -C ₁₄ alkyl group	0.6%		0.5%	0.6%		0.5%

(continued)

	Ingredient	A	B	C	D	E	F
5	Sodium C ₁₂₋₁₈ linear alkyl sulphate condensed with an average of 3 to 5 moles of ethylene oxide per mole of alkyl sulphate		2.0%	0.8%			
	Mid chain methyl branched sodium C ₁₂₋₁₈ linear alkyl sulphate				1.4%		1.0%
10	Sodium linear C ₁₂₋₁₈ linear alkyl sulphate				0.7%		0.5%
	Sodium tripolyphosphate (anhydrous weight given)	25%	30%	30%			
15	Citric acid				2.5%	2.0%	3.0%
	Sodium carboxymethyl cellulose	0.3%	0.2%		0.2%	0.2%	
	Hydrophobically modified (e.g. ester modified) cellulose				0.8%	0.7%	0.5%
20	Sodium polyacrylate polymer having a weight average molecular weight of from 3,000 to 5,000		0.5%	0.8%			
25	Copolymer of maleic/acrylic acid, having a weight average molecular weight of from 50,000 to 90,000, wherein the ratio of maleic to acrylic acid is from 1:3 to 1:4	-			1.4%	1.5%	
30	Sulphated or sulphonated bis((C ₂ H ₅ O)(C ₂ H ₄ O) _n)(CH ₃)N ⁺ C _x H _{2x} N ⁺ (CH ₃)bis(C ₂ H ₅ O)(C ₂ H ₄ O) _n), wherein n= from 20 to 30 and x = from 3 to 8		1.5%	1.0%		1.0%	1.5%
	Diethylene triamine pentaacetic acid	0.2%	0.3%	0.3%			
	Diethylene triamine pentaacetic acid				0.2%	0.3%	0.3%
35	Proteolytic enzyme having an enzyme activity of from 15mg/g to 70mg/g	0.5%	0.4%	0.5%	0.1%	0.15%	0.2%
	Amylolytic enzyme having an enzyme activity of from 25mg/g to 50mg/g	0.2%	0.3%	0.3%	0.2%	0.1%	0.15%
40	Anhydrous sodium perborate monohydrate	5%	4%	5%			
	Sodium percarbonate				6%	8%	6.5%
	Magnesium sulphate				0.4%	0.3%	0.3%
45	Nonanoyl oxybenzene sulphonate	2%	1.5%	1.7%			
	Tetraacetylenediamine	0.6%	0.8%	0.5%	1.2%	1.5%	1.0%
	Brightener	0.1 %	0.1 %	0.1 %	0.04%	0.03%	0.04%
	Sodium carbonate	25%	22%	25%	28%	28%	20%
50	Sodium sulphate	14%	14%	14%	12%	15%	10%
	Zeolite A	1%	1.5%	2%	20%	18%	22%
	Sodium silicate (2.0R)	0.8%	1%	1%			
	Crystalline layered silicate				3%	3.5%	4%
55	Photobleach	0.005%	0.004%	0.005%	0.001%	0.002%	0.002%
	Montmorillonite clay						10%

(continued)

Ingredient	A	B	C	D	E	F
Polyethyleneoxide having a weight average molecular weight of from 100,000 to 1,000,000						0.2%
Perfume particle according to example 2	3%	2%	1%	3%	2%	1%
Perfume spray-on		0.5%	0.3%		0.3%	0.5%
Starch encapsulated perfume accord			0.2%		0.2%	
Silicone based suds suppressor				0.05%	0.06%	0.05%
Miscellaneous and moisture	to 100%	To 100%	to 100%	to 100%	to 100%	to 100%

Example 4

[0052] The following perfume accord is an example of a spray-on perfume that is illustrative of a perfume component having a fabric delivery index for dry versus wet fabrics of less than 0.1, and which can be used in combination with the perfume particles of example 2. Amounts given below are by weight of the perfume accord.

PRM trade name	PRM chemical name	Amount
Intreleven aldehyde™	10 undecenal	0.2%
Ethyl safranate™	Ethyl 2,6,6-trimethyl-1,3-cyclohexadiene-1-carboxylate	2%
Keone		0.2%
Phenyl acetaldehyde	1-oxo-2-phenylethane	0.5%
Diphenyl oxide	Diphenyl ether	2.5%
Methyl Diantilis™	2-ethoxy-4-methoxymethylphenol	1.5%
Citronellyl acetate	3,7-dimethyl-6-octen-1-yl acetate	5%
Ionone 100%™	3-buten-2-one,4-(2,6,6-trimethyl-2-cyclohexen-1-yl)	15%
Phenyl ethyl alcohol	2-phenylethylalcohol	10%
Linalool	3,7-dimethyl-1,6-octadien-3-ol	15%
Vertenex	Para-tertiary-butylcyclohexylacetate	15%
Citronellol	3,7-dimethyl-6-octen-1-ol	20%
Hexyl salicylate	n-hexyl-ortho-hydroxybenzoate	13.1 %

[0053] This perfume accord is an example of a rose perfume accord.

Claims

1. A laundry additive composition comprising one or more perfume components in slow release form and wherein the release kinetics are controlled so as to provide a fabric delivery index for dry versus wet fabrics of at least 0.3.
2. A composition according to claim 1, wherein the one or more perfume components has a fabric delivery index of at least 0.5, preferably at least 0.7.
3. A composition according to any preceding claim additionally comprising at least one other perfume component of a different composition and olfactory character having a fabric delivery index for dry versus wet fabrics of less than 0.1, preferably less 0.05, more preferably less than 0.01.
4. A composition according to any preceding claim, wherein the perfume component is encapsulated with a water-

soluble or dispersible encapsulating agent.

5. A composition according to any preceding claim, wherein the perfume component is absorbed on a porous carrier material; preferably the porous carrier material is an aluminosilicate.
6. A laundry detergent composition comprising the laundry additive composition of any preceding claim.
7. A laundry detergent composition according to claim 6 comprising from 0wt% to 26wt% phosphate.
8. A process for preparing a solid perfume particle suitable for use in laundering, the process comprises the steps of:
 - a) contacting a perfume component with a porous carrier material, to form a perfume-loaded material; and
 - b) contacting the perfume-loaded material with an aqueous solution or dispersion of encapsulating material, to form an intermediate mixture; and
 - c) drying of the intermediate mixture to form a perfume particle,wherein, the perfume-loaded material is in contact with the aqueous solution or dispersion of encapsulating material for a period of time of less than 120 minutes prior to drying.
9. A process according to claim 8, wherein, in step (b), the perfume-loaded material is in contact with the aqueous solution or dispersion of encapsulating material for a period of time of less than 30 minutes, preferably less than 20 minutes.
10. A process according to any of claims 8-9, wherein step (b) is carried out at a temperature of less than 50°C, preferably less than 20°C.
11. A process according to any of claims 8-10, wherein, step (b) occurs in a low shear mixer.
12. A process according to any of claims 8-11, wherein, in step (c), the perfume-loaded material is spray dried in a spray-drying tower, and wherein further, the difference in temperature between the inlet air temperature and the outlet air temperature in the spray-drying tower is less than 100°C, preferably less than 80°C.
13. A perfume particle obtainable by any of the processes of claims 8-12, wherein the particle has release kinetics such that it provides a fabric delivery index of at least 0.3.
14. A laundry composition comprising a particle according to claim 13.
15. A method of perfuming a fabric, comprising the step of contacting a composition according to any of claims 1-3, 7 and 14, with a fabric.
16. A method of perfuming a fabric, comprising the step of contacting a perfume particle according to any of claims 4-6 and 13, with a fabric.
17. Use of a composition according to any of claims 1-3, 7 and 14, to give a dry fabric odour benefit to a fabric.
18. Use of a perfume particle according to any of claims 4-6 and 13, to give a dry fabric odour benefit to a fabric.



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PARTIAL EUROPEAN SEARCH REPORT

Application Number

which under Rule 45 of the European Patent Convention EP 02 25 5540 shall be considered, for the purposes of subsequent proceedings, as the European search report

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			C11D
INCOMPLETE SEARCH			
<p>The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.</p> <p>Claims searched completely :</p> <p>Claims searched incompletely :</p> <p>Claims not searched :</p> <p>Reason for the limitation of the search:</p> <p>see sheet C</p>			
Place of search:		Date of completion of the search	Examiner
THE HAGUE		28 January 2003	Neys, P
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (3.92) (9/04/07)



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INCOMPLETE SEARCH
SHEET C

Application Number
EP 02 25 5540

Claim(s) searched completely:
8-12

Claim(s) searched incompletely:
1-7, 13-18

Reason for the limitation of the search:

Present claims 1, 6, 13-18 and their dependent claims relate to a laundry additive or detergent composition and its use, a perfume particle and its use or a method of perfuming defined by reference to the following parameter:

- the fabric delivery index for dry versus wet fabrics

The use of this parameter in the present context is considered to lead to a lack of clarity within the meaning of Article 84 EPC. It is impossible to compare the parameter the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to:

- a laundry additive or detergent composition and a perfume particle comprising a perfume component which is either encapsulated with a water-soluble or dispersible encapsulating agent and/or absorbed on a porous carrier material (see claims 4 and 5).



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PARTIAL EUROPEAN SEARCH REPORT

Application Number

EP 02 25 5540

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(54) **Encapsulated fragrance chemicals**

(57) A polymeric encapsulated fragrance is disclosed which is suitable for use in personal care and cleaning products. In a preferred embodiment of the invention, the fragrance is encapsulated by a first polymer material to form a fragrance encapsulated polymer, the

polymer encapsulated shell is then coated with a polyamine polymer in a preferred embodiment the coating polymers are a reaction product of polyamines and (chloromethyl) oxirane or (bromomethyl) oxirane.

EP 1 407 753 A1

Description**Field of the Invention**

5 [0001] The present invention relates to fragrance materials that are encapsulated with a polymeric material, the encapsulated fragrance materials are further coated with a cationic polymer material. The encapsulated fragrance materials are well suited for rinse-off applications associated with personal care and cleaning products.

Background of the Invention

10 [0002] Fragrance chemicals are used in numerous products to enhance the consumer's enjoyment of a product. Fragrance chemicals are added to consumer products such as laundry detergents, fabric softeners, soaps, detergents, personal care products, such as shampoos, body washes, deodorants and the like, as well as numerous other products.

15 [0003] In order to enhance the effectiveness of the fragrance materials for the user, various technologies have been employed to enhance the delivery of the fragrance materials at the desired time. One widely used technology is encapsulation of the fragrance material in a protective coating. Frequently the protective coating is a polymeric material. The polymeric material is used to protect the fragrance material from evaporation, reaction, oxidation or otherwise dissipating prior to use. A brief overview of polymeric encapsulated fragrance materials is disclosed in the following U.S. Patents: U.S. Patent No. 4,081,384 discloses a softener or anti-stat core coated by a polycondensate suitable for use in a fabric conditioner; U.S. Patent No. 5,112,688 discloses selected fragrance materials having the proper volatility to be coated by coacervation with micro particles in a wall that can be activated for use in fabric conditioning; U.S. Patent No. 5,145,842 discloses a solid core of a fatty alcohol, ester, or other solid plus a fragrance coated by an aminoplast shell; and U.S. Patent No. 6,248,703 discloses various agents including fragrance in an aminoplast shell that is included in an extruded bar soap.

25 [0004] While encapsulation of fragrance in a polymeric shell can help prevent fragrance degradation and loss, it is often not sufficient to significantly improve fragrance performance in consumer products. Therefore, methods of aiding the deposition of encapsulated fragrances have been disclosed. U.S. Patent No. 4,234,627 discloses a liquid fragrance coated with an aminoplast shell further coated by a water insoluble meltable cationic coating in order to improve the deposition of capsules from fabric conditioners. U.S. Patent No. 6,194,375 discloses the use of hydrolyzed polyvinyl alcohol to aid deposition of fragrance-polymer particles from wash products. U.S. Patent No. 6,329,057 discloses use of materials having free hydroxy groups or pendant cationic groups to aid in the deposition of fragranced solid particles from consumer products.

30 [0005] Despite these and many other disclosures there is an ongoing need for the improved delivery of fragrance materials for various rinse-off products that provide improved performance.

Summary of the Invention

35 [0006] The present invention is directed to a polymer encapsulated fragrance, the polymer encapsulated fragrance being further treated with a cationic polymer to improve deposition. More specifically the present invention is directed to a composition comprising:

40 [0007] A fragrance material; said fragrance material encapsulated by a polymer to create a polymer encapsulated fragrance; the polymer encapsulated fragrance being further coated by a cationic polymer. In a preferred embodiment of the invention the cationic polymer is selected from the group consisting of cationic polyamide and a cationic heterocyclic compound and mixtures thereof. In a highly preferred embodiment of the invention the cationic material comprises 1H-imidazole polymer with (chloromethyl oxirane) and 1,6 hexanediamine, N-(6-aminoethyl)-polymer with (chloromethyl) oxirane. In particular, reaction products of 1H-imidazole and (chloromethyl) oxirane, known under Chemical Abstract Service number (CAS) 68797-57-9. Also preferred is a polymer comprising 1,6-hexanediamine, N-(6-aminoethyl) with (chloromethyl) oxirane, known under CAS number 67953-56-4. These materials are available Regency Chemicals, Leics, England. A method for making the cationic coated polymer encapsulated fragrances is also disclosed.

50 [0008] The present invention is well suited for use in rinse off products, which are products that are applied to a substrate and then removed in some manner. Especially preferred products that use the cationic coated polymer encapsulated fragrance of the present invention include, without limitation, hair and pet shampoos, hair conditioners, laundry detergents, fabric conditioners and the like. These and other embodiments of the present invention will become apparent upon referring to the following figure and description of the invention.

Detailed Description of the Invention

55 [0009] The fragrances suitable for use in this invention include without limitation, any combination of fragrance,

essential oil, plant extract or mixture thereof that is compatible with, and capable of being encapsulated by a polymer.

[0010] Many types of fragrances can be employed in the present invention, the only limitation being the compatibility and ability to be encapsulated by the polymer being employed, and compatibility with the encapsulation process used. Suitable fragrances include but are not limited to fruits such as almond, apple, cherry, grape, pear, pineapple, orange, strawberry, raspberry; musk, flower scents such as lavender-like, rose-like, iris-like, and carnation-like. Other pleasant scents include herbal scents such as rosemary, thyme, and sage; and woodland scents derived from pine, spruce and other forest smells. Fragrances may also be derived from various oils, such as essential oils, or from plant materials such as peppermint, spearmint and the like. Other familiar and popular smells can also be employed such as baby powder, popcorn, pizza, cotton candy and the like in the present invention.

[0011] A list of suitable fragrances is provided in U.S. Patents 4,534,891, 5,112,688 and 5,145,842. Another source of suitable fragrances is found in *Perfumes Cosmetics and Soaps*, Second Edition, edited by W. A. Poucher, 1959. Among the fragrances provided in this treatise are acacia, cassie, chypre, cynamen, fern, gardenia, hawthorn, heliotrope, honeysuckle, hyacinth, jasmine, lilac, lily, magnolia, mimosa, narcissus, freshly-cut hay, orange blossom, orchids, reseda, sweet pea, trefle, tuberose, vanilla, violet, wallflower, and the like.

[0012] As used herein olfactory effective amount is understood to mean the amount of compound in perfume compositions the individual component will contribute to its particular olfactory characteristics, but the olfactory effect of the fragrance composition will be the sum of the effects of each of the fragrance ingredients. Thus the compounds of the invention can be used to alter the aroma characteristics of the perfume composition by modifying the olfactory reaction contributed by another ingredient in the composition. The amount will vary depending on many factors including other ingredients, their relative amounts and the effect that is desired.

[0013] The level of fragrance in the cationic polymer coated encapsulated fragrance varies from about 5 to about 95 weight percent, preferably from about 40 to about 95 and most preferably from about 50 to about 90 weight percent on a dry basis. In addition to the fragrance other agents can be used in conjunction with the fragrance and are understood to be included.

[0014] As noted above, the fragrance may also be combined with a variety of solvents which serve to increase the compatibility of the various materials, increase the overall hydrophobicity of the blend, influence the vapor pressure of the materials, or serve to structure the blend. Solvents performing these functions are well known in the art and include mineral oils, triglyceride oils, silicone oils, fats, waxes, fatty alcohols, and diethyl phthalate among others.

[0015] A common feature of many encapsulation processes is that they require the fragrance material to be encapsulated to be dispersed in aqueous solutions of polymers, pre-condensates, surfactants, and the like prior to formation of the capsule walls. Therefore, materials having low solubility in water, such as highly hydrophobic materials are preferred, as they will tend to remain in the dispersed perfume phase and partition only slightly into the aqueous solution. Fragrance materials with Clog P values greater than 1, preferably greater than 3, and most preferably greater than 5 will thus result in microcapsules that contain cores most similar to the original composition, and will have less possibility of reacting with materials that form the capsule shell.

[0016] One object of the present invention is to deposit capsules containing fragrance cores on desired substrates such as cloth, hair, and skin during washing and rinsing processes. Further, it is desired that, once deposited, the capsules release the encapsulated fragrance either by diffusion through the capsule wall, via small cracks or imperfections in the capsule wall caused by drying, physical, or mechanical means, or by large-scale rupture of the capsule wall. In each of these cases, the volatility of the encapsulated perfume materials is critical to both the speed and duration of release, which in turn control consumer perception. Thus, fragrance chemicals which have higher volatility as evidenced by normal boiling points of less than 250°C, preferably less than about 225°C are preferred in cases where quick release and impact of fragrance is desired. Conversely, fragrance chemicals that have lower volatility (boiling points greater than 225°C) are preferred when a longer duration of aroma is desired. Of course, fragrance chemicals having varying volatility may be combined in any proportions to achieve the desired speed and duration of perception.

[0017] In order to provide the highest fragrance impact from the fragrance encapsulated capsules deposited on the various substrates referenced above, it is preferred that materials with a high odor-activity be used. Materials with high odor-activity can be detected by sensory receptors at low concentrations in air, thus providing high fragrance perception from low levels of deposited capsules. This property must be balanced with the volatility as described above. Some of the principles mentioned above are disclosed in U.S. Patent No. 5,112,688.

[0018] Further, it is clear that materials other than fragrances may be employed in the system described here. Examples of other materials which may be usefully deposited from rinse-off products using the invention include sunscreens, softening agents, insect repellents, and fabric conditioners, among others.

[0019] Encapsulation of fragrances is known in the art, see for example U.S. Patent Nos. 2,800,457, 3,870,542, 3,516,941, 3,415,758, 3,041,288, 5,112,688, 6,329,057, and 6,261,483. Another discussion of fragrance encapsulation is found in the *Kirk-Othmer Encyclopedia*.

[0020] Preferred encapsulating polymers include those formed from melamine-formaldehyde or urea-formaldehyde condensates, as well as similar types of aminoplasts. Additionally, capsules made via the simple or complex coacer-

vation of gelatin are also preferred for use with the coating. Capsules having shell walls comprised of polyurethane, polyamide, polyolefin, polysaccharide, protein, silicone, lipid, modified cellulose, gums, polyacrylate, polyphosphate, polystyrene, and polyesters or combinations of these materials are also functional.

[0021] A representative process used for aminoplast encapsulation is disclosed in U.S. Patent No. 3,516,941 though it is recognized that many variations with regard to materials and process steps are possible. A representative process used for gelatin encapsulation is disclosed in U.S. Patent No. 2,800,457 though it is recognized that many variations with regard to materials and process steps are possible. Both of these processes are discussed in the context of fragrance encapsulation for use in consumer products in U.S. Patent Nos. 4,145,184 and 5,112,688 respectively.

[0022] Well known materials such as solvents, surfactants, emulsifiers, and the like can be used in addition to the polymers described above to encapsulate the fragrance without departing from the scope of the present invention. It is understood that the term encapsulated is meant to mean that the fragrance material is substantially covered in its entirety. Encapsulation can provide pore vacancies or interstitial openings depending on the encapsulation techniques employed. More preferably the entire fragrance material portion of the present invention is encapsulated.

[0023] Particles comprised of fragrance and a variety of polymeric and non-polymeric matrixing materials are also suitable for use. These may be composed of polymers such as polyethylene, fats, waxes, or a variety of other suitable materials. Essentially any capsule, particle, or dispersed droplet may be used that is reasonably stable in the application and release of fragrance at an appropriate time once deposited.

[0024] Particle and capsule diameter can vary from about 10 nanometers to about 1000 microns, preferably from about 50 nanometers to about 100 microns and most preferably from about 2 to about 15 microns. The capsule distribution can be narrow, broad, or multimodal. Multi-modal distributions may be composed of different types of capsule chemistries.

[0025] Once the fragrance material is encapsulated a cationically charged water-soluble polymer is applied to the fragrance encapsulated polymer. This water-soluble polymer can also be an amphoteric polymer with a ratio of cationic and anionic functionalities resulting in a net total charge of zero and positive, i.e., cationic. Those skilled in the art would appreciate that the charge of these polymers can be adjusted by changing the pH, depending on the product in which this technology is to be used. Any suitable method for coating the cationically charged materials onto the encapsulated fragrance materials can be used. The nature of suitable cationically charged polymers for assisted capsule delivery to interfaces depends on the compatibility with the capsule wall chemistry since there has to be some association to the capsule wall. This association can be through physical interactions, such as hydrogen bonding, ionic interactions, hydrophobic interactions, electron transfer interactions or, alternatively, the polymer coating could be chemically (covalently) grafted to the capsule or particle surface. Chemical modification of the capsule or particle surface is another way to optimize anchoring of the polymer coating to capsule or particle surface. Furthermore, the capsule and the polymer need to want to go to the desired interface and, therefore, need to be compatible with the chemistry (polarity, for instance) of that interface. Therefore, depending on which capsule chemistry and interface (e.g., cotton, polyester, hair, skin, wool) is used the cationic polymer can be selected from one or more polymers with an overall zero (amphoteric: mixture of cationic and anionic functional groups) or net positive charge, based on the following polymer backbones: polysaccharides, polypeptides, polycarbonates, polyesters, polyolefinic (vinyl, acrylic, acrylamide, poly diene), polyester, polyether, polyurethane, polyoxazoline, polyamine, silicone, polyphosphazine, olyaromatic, poly heterocyclic, or polyionene, with molecular weight (MW) ranging from about 1,000 to about 1000,000,000, preferably from about 5,000 to about 10,000,000. As used herein molecular weight is provided as weight average molecular weight. Optionally, these cationic polymers can be used in combination with nonionic and anionic polymers and surfactants, possibly through coacervate formation.

[0026] A more detailed list of cationic polymers that can be used to coat the encapsulated fragrance is provided below:

Polysaccharides include but are not limited to guar, alginates, starch, xanthan, chitosan, cellulose, dextrans, arabic gum, carrageenan, hyaluronates. These polysaccharides can be employed with:

(a) cationic modification and alkoxy-cationic modifications, such as cationic hydroxyethyl, cationic hydroxy propyl. For example, cationic reagents of choice are 3-chloro-2-hydroxypropyl trimethylammonium chloride or its epoxy version. Another example is graft-copolymers of polyDADMAC on cellulose like in Celquat L-200 (Polyquaternium-4), Polyquaternium-10 and Polyquaternium-24, commercially available from National Starch, Bridgewater, N.J.;

(b) aldehyde, carboxyl, succinate, acetate, alkyl, amide, sulfonate, ethoxy, propoxy, butoxy, and combinations of these functionalities. Any combination of Amylose and Mylopectin and overall molecular weight of the polysaccharide; and

(c) any hydrophobic modification (compared to the polarity of the polysaccharide backbone).

[0027] The above modifications described in (a), (b) and (c) can be in any ratio and the degree of functionalization

up to complete substitution of all functionalizable groups, and as long as the theoretical net charge of the polymer is zero (mixture of cationic and anionic functional groups) or preferably positive. Furthermore, up to 5 different types of functional groups may be attached to the polysaccharides. Also, polymer graft chains may be differently modified than the backbone. The counterions can be any halide ion or organic counter ion. U.S. Patent Nos. 6,297,203 and U.S. 6,200,554.

[0028] Another source of cationic polymers contain protonatable amine groups so that the overall net charge is zero (amphoteric; mixture of cationic and anionic functional groups) or positive. The pH during use will determine the overall net charge of the polymer. Examples are silk protein, zein, gelatin, keratin, collagen and any polypeptide, such as polylysine.

[0029] Further cationic polymers include poly vinyl polymers, with up to 5 different types of monomers, having the monomer generic formula $-C(R_2)(R_1)-CR_2R_3-$. Any co-monomer from the types listed in this specification may also be used. The overall polymer will have a net theoretical positive charge or equal to zero (mixture of cationic and anionic functional groups). Where R1 is any alkanes from C1-C25 or H; the number of double bonds ranges from 0-5. Furthermore, R1 can be an alkoxylated fatty alcohol with any alkoxy carbon-length, number of alkoxy groups and C1-C25 alkyl chain length. R1 can also be a liquid crystalline moiety that can render the polymer thermotropic liquid crystalline properties, or the alkanes selected can result in side-chain melting. In the above formula R2 is H or CH3; and R3 is -Cl, -NH2, -NHR1, -NR1R2, -NR1R2 R6 (where R6 = R1, R2, or -CH2-COOH or its salt), -NH-C(O)-H, -C(O)-NH2 (amide), -C(O)-N(R2)(R2')(R2''), -OH, styrene sulfonate, pyridine, pyridine-N-oxide, quaternized pyridine, imidazolium halide, imidazolium halide, imidazol, piperidine, pyrrolidone, alkyl-substituted pyrrolidone, caprolactam or pyridine, phenyl-R4 or naphthalene-R5 where R4 and R5 are R1, R2, R3, sulfonic acid or its alkali salt -COOH, -COO- alkali salt, ethoxy sulphate or any other organic counter ion. Any mixture or these R3 groups may be used. Further suitable cationic polymers containing hydroxy alkyl vinyl amine units, as disclosed in U.S. Patent No 6,057,404.

[0030] Another class of materials are polyacrylates, with up to 5 different types of monomers, having the monomer generic formula: $-CH(R_1)-C(R_2)(CO-R_3-R_4)-$. Any co-monomer from the types listed in this specification may also be used. The overall polymer will have a net theoretical positive charge or equal to zero (mixture of cationic and anionic functional groups). In the above formula R1 is any alkane from C1-C25 or H with number of double bonds from 0-5, aromatic moieties, polysiloxane, or mixtures thereof. Furthermore, R1 can be an alkoxylated fatty alcohol with any alkoxy carbon-length, number of alkoxy groups and C1-C25 alkyl chain length. R1 can also be a liquid crystalline moiety that can render the polymer thermotropic liquid crystalline properties, or the alkanes selected can result in side-chain melting. R2 is H or CH3; R3 is alkyl alcohol C1-25 or an alkylene oxide with any number of double bonds, or R3 may be absent such that the C=O bond is (via the C-atom) directly connected to R4. R4 can be: -NH2, NHR1, -NR1R2, -NR1R2 R6 (where R6 = R1, R2, or -CH2-COOH or its salt), -NH-C(O)-, sulfo betaine, betaine, polyethylene oxide, poly(ethyleneoxide/propylene oxide/butylene oxide) grafts with any end group, H, OH, styrene sulfonate, pyridine, quaternized pyridine, alkyl-substituted pyrrolidone or pyridine, pyridine-N-oxide, imidazolium halide, imidazolium halide, imidazol, piperidine, -OR1, -OH, -COOH alkali salt, sulfonate, ethoxy sulphate, pyrrolidone, caprolactam, phenyl-R4 or naphthalene-R5 where R4 and R5 are R1, R2, R3, sulfonic acid or its alkali salt or organic counter ion. Any mixture or these R3 groups may be used. Also, glyoxylated cationic polyacrylamides can be used. Typical polymers of choice are those containing the cationic monomer dimethylaminoethyl methacrylate (DMAEMA) or methacrylamidopropyl trimethyl ammonium chloride (MAPTAC). DMAEMA can be found in Gafquat and Gaffix VC-713 polymers from ISP. MAPTAC can be found in BASF's Luviquat PQ11 PN and ISP's Gafquat HS100.

[0031] Another group of polymers that can be used are those that contain cationic groups in the main chain or backbone. Included in this group are:

(1) polyalkylene imines such as polyethylene imine, commercially available as Lupasol from BASF. Any molecular weight and any degree of crosslinking of this polymer can be used in the present invention;

(2) ionenes having the general formula set forth as

$-[N(+)R1R2-A1-N(RS)-X-N(R6)-A2-N(+)R3R4-A3]_n-2Z-$, as disclosed in U.S. Patent Nos. 4,395,541 and U.S. 4,597,962;

(3) adipic acid/dimethyl amino hydroxypropyl diethylene triamine copolymers, such as Cartaretin F-4 and F-23, commercially available from Sandoz;

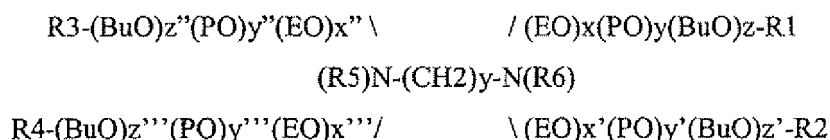
(4) polymers of the general formula $-[N(CH_3)_2-(CH_2)_x-NH-(CO)-NH-(CH_2)_y-N(CH_3)_2-(CH_2)_z-O-(CH_2)_p]_n-$, with x, y, z, p=1-12, and n according to the molecular weight requirements. Examples are Polyquaternium 2 (Mirapol A-15), Polyquaternium-17 (Mirapol AD-1), and Polyquaternium-18 (Mirapol AZ-1).

[0032] Other polymers include cationic polysiloxanes and cationic polysiloxanes with carbon-based grafts with a net theoretical positive charge or equal to zero (mixture of cationic and anionic functional groups). This includes cationic end-group functionalized silicones (i.e. Polyquaternium-80). Silicones with general structure: $-[Si(R_1)(R_2)-O]_x-[Si(R_3)(R_2)-O]_y-$ where R1 is any alkane from C1-C25 or H with number of double bonds from 0-5, aromatic moieties,

polysiloxane grafts, or mixtures thereof. R1 can also be a liquid crystalline moiety that can render the polymer thermotropic liquid crystalline properties, or the alkanes selected can result in side-chain melting. R2 can be H or CH3 and R3 can be -R1-R4, where R4 can be -NH2, -NHR1, -NR1R2, -NR1R2R6 (where R6 = R1, R2, or -CH2-COOH or its salt), -NH-C(O)-, -COOH, -COO- alkali salt, any C1-25 alcohol, -C(O)-NH2 (amide), -C(O)-N(R2)(R2')(R2''), sulfo betaine, betaine, polyethylene oxide, poly(ethyleneoxide/propylene oxide/butylene oxide) grafts with any end group, H,-OH, styrene sulfonate, pyridine, quaternized pyridine, alkyl-substituted pyrrolidone or pyridine, pyridine-N-oxide, imidazolinium halide, imidazolium halide, imidazol, piperidine, pyrrolidone, caprolactam, -COOH, -COO- alkali salt, sulfonate, ethoxy sulphate phenyl-R5 or naphthalene-R6 where R5 and R6 are R1, R2, R3, sulfonic acid or its alkali salt or organic counter ion. R3 can also be -(CH2)x-O-CH2-CH(OH)-CH2-N(CH3)2-CH2-COOH and its salts. Any mixture of these R3 groups can be selected. X and y can be varied as long as the theoretical net charge of the polymer is zero (amphoteric) or positive. In addition, polysiloxanes containing up to 5 different types of monomeric units may be used. Examples of suitable polysiloxanes are found in U.S. Patent Nos. 4,395,541 4,597,962 and U.S.6,200,554. Another group of polymers that can be used to improve capsule/particle deposition are phospholipids that are modified with cationic polysiloxanes. Examples of these polymers are found in U.S. Patent No. 5,849,313 and WO Patent Application 9518096A1 and European Patent EP0737183B1.

[0033] Furthermore, copolymers of silicones and polysaccharides and proteins can be used (commercially available as CRODASONE brand products).

[0034] Another class of polymers include polyethylene oxide-co-propyleneoxide-co-butylene oxide polymers of any ethylene oxide/propylene oxide / butylene oxide ratio with cationic groups resulting in a net theoretical positive charge or equal to zero (amphoteric). The general structure is:



where R1,2,3,4 is -NH2, -N(R)3- X+, R with R being H or any alkyl group. R5,6 is -CH3 or H. Counter ions can be any halide ion or organic counter ion. X, Y, may be any integer, any distribution with an average and a standard deviation and all 12 can be different. Examples of such polymers are the commercially available TETRONIC brand polymers.

[0035] Suitable polyheterocyclic (the different molecules appearing in the backbone) polymers include the piperazine-alkylene main chain copolymers disclosed in Ind. Eng. Chem. Fundam., (1986), 25, pp.120-125, by Isamu Kashi and Akira Suzuki.

[0036] Also suitable for use in the present invention are copolymers containing monomers with cationic charge in the primary polymer chain. Up to 5 different types of monomers may be used. Any co-monomer from the types listed in this specification may also be used. Examples of such polymers are poly diallyl dimethyl ammonium halides (Poly-DADMAC) copolymers of DADMAC with vinyl pyrrolidone, acrylamides, imidazoles, imidazolinium halides, etc. These polymers are disclosed in Henkel EP0327927A2 and PCT Patent Application 01/62376A1. Also suitable are Poly-quaternium-6 (Merquat 100), Polyquaternium-7 (Merquats S, 550, and 2200), Polyquaternium-22 (Merquats 280 and 295) and Polyquaternium-39 (Merquat Plus 3330), available from Onco Nalco.

[0037] Polymers containing non-nitrogen cationic monomers of the general type -CH2-C(R1)(R2-R3-R4)- can be used with: R1 being a -H or C1-C20 hydrocarbon. R2 is a disubstituted benzene ring or an ester, ether, or amide linkage. R3 is a C1-C20 hydrocarbon, preferably C1-C10, more preferably C1-C4. R4 can be a trialkyl phosphonium, dialkyl sulfonium, or a benzopyrillium group, each with a halide counter ion. Alkyl groups for R4 are C1-C20 hydrocarbon, most preferably methyl and t-butyl. These monomers can be copolymerized with up to 5 different types of monomers. Any co-monomer from the types listed in this specification may also be used.

[0038] Substantivity of these polymers may be further improved through formulation with cationic, amphoteric and nonionic surfactants and emulsifiers, or by coacervate formation between surfactants and polymers or between different polymers. Combinations of polymeric systems (including those mentioned previously) may be used for this purpose as well as those disclosed in EP1995/000400185.

[0039] Furthermore, polymerization of the monomers listed above into a block, graft or star (with various arms) polymers can often increase the substantivity toward various surfaces. The monomers in the various blocks, graft and arms can be selected from the various polymer classes listed in this specification.

[0040] Polymers, or mixtures of the following polymers:

(a) Polymers comprising reaction products between polyamines and (chloromethyl) oxirane or (bromomethyl) ox-

irane. Polyamines being $2(R_1)N-[R_2-N(R_1)]_n-R_2-N(R_1)_2$, $2HN-R_1-NH_2$, $2HN-R_2-N(R_1)_2$ and 1H-Imidazole. Also, the polyamine can be melamine. R_1 in the polyamine being H or methyl. R_2 being alkylene groups of C1-C20 or phenylene groups. Examples of such polymers are known under the CAS numbers 67953-56-4 and 68797-57-9. The ratio of (chloromethyl) oxirane to polyamine in the cationic polymer ranges from 0.05-0.95.

(b) Polymers comprising reaction products of alkanedioic acids, polyamines and (chloromethyl) oxirane or (bromomethyl) oxirane. Alkane groups in alkanedioic acids C0-C20. Polyamine structures are as mentioned in (a). Additional reagents for the polymer are dimethyl amine, aziridine and polyalkylene oxide (of any molecular weight but, at least, di-hydroxy terminated; alkylene group being C1-20, preferably C2-4). The polyalkylene oxide polymers that can also be used are the Tetronics series. Examples of polymers mentioned here are known under the CAS numbers 68583-79-9 (additional reagent being dimethyl amine), 96387-48-3 (additional reagent being urea), and 167678-45-7 (additional reagents being polyethylene oxide and aziridine). These reagents can be used in any ratio. (c) Polyamido Amine and Polyaminoamide-epichlorohydrin resins, as described by David Devore and Stephen Fisher in Tappi Journal, vol.76, No.8, pp. 121-128 (1993). Also referenced herein is "Polyamide-polyamine-epichlorohydrin resins" by W. W. Moyer and R. A. Stagg in Wet-Strength in Paper and Paperboard, Tappi Monograph Series No. 29, Tappi Press (1965), Ch.3, 33-37.

[0041] The preferred cationically charged materials comprise reaction products of polyamines and (chloromethyl) oxirane. In particular, reaction products of 1H-imidazole and (chloromethyl) oxirane, known under CAS number 68797-57-9. Also preferred are polymers comprising reaction products of 1,6-hexanediamine, N-(6-aminoethyl) and (chloromethyl) oxirane, known under CAS number 67953-56-4. The preferred weight ratio of the imidazole polymer and the hexanediamine, amino hexyl polymer is from about 5:95 to about 95:5 weight percent and preferably from about 25:75 to about 75:25.

[0042] The level of outer cationic polymer is from about 1% to about 3000%, preferably from about 5% to about 1000% and most preferably from about 10% to about 500% of the fragrance containing compositions, based on a ratio with the fragrance on a dry basis.

[0043] The weight ratio of the encapsulating polymer to fragrance is from about 1:25 to about 1:1. Preferred products have had the weight ratio of the encapsulating polymer to fragrance varying from about 1:10 to about 4:96.

[0044] For example, if a capsule blend has 20 weight % fragrance and 20 weight % polymer, the polymer ratio would be (20/20) multiplied by 100 (%) = 100%.

[0045] The present invention, the encapsulated fragrance is well suited for wash-off products. Wash-off products are understood to be those products that are applied for a given period of time and then are removed. These products are common in areas such as laundry products, and include detergents, fabric conditioners, and the like; as well as personal care products which include shampoos, hair rinses, body washes, soaps and the like.

[0046] We have discovered that the present invention is advantageously applied to products, including fabric rinse conditioners, having a pH of less than 7, preferably less than about 5 and most preferably less than about 4.

[0047] A better product, including wash-off products such as fabric rinse conditioner is also obtained when the salt level is limited. The improvement in the fabric rinse conditioner is noted by a longer lasting and/or improved delivery of fragrance. One method of improving the delivery of the encapsulated fragrance is to limit the amount of salt in the product base. Preferably the level of salt in the rinse conditioner product is less than or equal to about 1 weight percent by weight in the product, preferably less than about 0.5 weight percent and most preferably less than about 0.1 weight percent.

[0048] More specifically we have discovered that limiting the level of calcium chloride will improve the delivery of the fragrance using the encapsulated fragrance of the present invention. Improved fragrance delivery is provided by limiting the amount of calcium chloride to less than about 2 weight percent, typically less than 1 weight percent and more preferably less than 0.5 weight percent. As it is known in the art, calcium chloride is added to control viscosity of the formulations, so there is trade-off between the viscosity and fragrance delivery. We have discovered suitable formulations with calcium chloride levels of from about 0.05 to about 1 weight percent of the formulation, preferably from about 0.1 to about 0.7 and most preferably from about 0.25 to about 0.5 weight percent of the formulation. We have discovered that limiting the level of calcium chloride level as set forth above is particularly advantageous in fabric rinse conditioner products.

[0049] Another means for improving the performance of delivery of the encapsulated fragrance of the present invention is to limit the level of some softening agents. We have discovered that limiting the softening actives, such as triethanolamine quaternary, diethanolamine quaternary, ACCOSOF cationic surfactants (Stepan Chemical), or ditalow dimethyl ammonium chloride (DTDMAC), to an amount of from about 5 to about 30 weight percent of the product, preferably from about 10 to about 20 and more preferably from about 12 to 14 weight percent of a fabric rinse conditioner product will improve the performance of the fragrance. The above softening agents are well known in the art and are disclosed in U.S. Patents 6,521,589 and 6,180,594.

[0050] Yet another means for improving fragrance delivery of the present invention is to limit the level of the non-

ionic surfactants employed in the product, including a fabric softening product. Many non-ionic surfactants are known in the art and include alkyl ethoxylate, commercially available as NEODOL (Shell Oil Company), nonyl phenol ethoxylate, TWEEN surfactants (ICI Americas Inc.), and the like. We have discovered that the encapsulated fragrance of the present invention are advantageously used when the non-ionic surfactant level is below about 5 weight percent of the product, preferably less than about 1 weight percent and most preferably less than 0.5 weight percent.

[0051] Yet another means for enhancing the fabric softener product is to limit the level of co-solvent included in the fabric softener in addition to water. Reducing the level of co-solvents such as ethanol and isopropanol to less than about 5 weight percent of the product, preferably less than about 2 and most preferably less than about 1 weight percent of the fabric softener product has been found to improve fragrance delivery.

[0052] Improved fragrance performance includes longer lasting fragrance, improved substantivity of the fragrance on cloth or the ability to provide improved fragrance notes, such as specific fragrance notes through the use of the present invention.

[0053] While the above description is primarily to fabric rinse conditioner products, additional studies for shampoos, detergent and other cleaning products have also led to preferred embodiments for these products as well.

[0054] As was found for fabric rinse conditioners, additional studies have determined that lower pH is desirable for the delivery of fragrance when used in the product base. The preferred bases are neutral or mildly acidic, preferably having a pH of 7, more preferably less than about 5 and most preferably less than about 4 for shampoos, detergent and other cleaning products.

[0055] We have found that powder detergent and other cleaning products provide enhanced fragrance delivery when the material coating the encapsulating polymer is also neutral or slightly acidic. Preferred materials are NaHSO₄, acetic acid, citric acid and other similar acidic materials and their mixtures. These materials have a pH of less than about 7, preferably less than about 5 and most preferably less than about 4.

[0056] As was described with fabric rinse conditioners, lower surfactant levels were advantageously employed in shampoos, detergents and other cleaning products bases with the present invention. The level of surfactant is preferably less than about 30, more preferably less than about 20 and most preferably less than about 10 weight percent of the product base. A similar finding was found with preferred levels of salt in shampoos, detergents and other cleaning products as was found in fabric rinse conditioners. The salt level is preferably less than about 5 weight percent, more preferably less than about 2 and most preferably less than 0.5 weight percent of the product.

[0057] Lower solvent levels found in the base improves the fragrance delivery in shampoos, detergents and other cleaning products as well. Solvents, include but are not limited to, ethanol, isopropanol, dipropylene glycol in addition to the water base and the hydrotope level is preferably less than 5 weight percent, preferably less than about 2 and most preferably less than 1 weight percent of the total product base.

[0058] A preferred surfactant base for shampoos, detergents and other cleaning products was found to be ethoxylated surfactants such as alkyl ethoxylated sulfates, (C₁₂-C₁₄)(ethylene oxide)_nSO₄M; or ethoxylated carboxylate surfactants (C₁₂-C₁₄)(Ethylene oxide)_nCOOM where n is from 1 to about 15 and M is Na⁺, K⁺ or NH₄⁺ cation. A more preferred class of surfactants for use in the present invention was zwitterionic surfactants such as the alkyl amine oxides, taurides, betaines and sulfobetaines. Zwitterionic surfactants are disclosed in greater detail in U.S. Patent 6,569,826. Other commercially available surfactants are AMPHOSOL series of betaines (Stepan Chemical); TEGO-TIAN by Goldschmidt; and HOSTAPAN and ARKOPAN by Clariant.

[0059] The most preferred surfactant system to be employed with the encapsulated fragrance system of the present invention was found to be non-ionic surfactants. Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C₈-C₂₀ aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C₁₀-C₁₅ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide). These nonionic surfactants are disclosed in U.S. Patent 6,517,588.

[0060] Polymers that are known as deposition aids, and in a preferred embodiment are also cationic can be found in the following resources:

Encyclopedia of Polymers and Thickeners for Cosmetics, Robert Lochhead and William From, in Cosmetics & Toiletries, Vol. 108, May 1993, pp. 95-138;

Modified Starches: Properties & Uses, O. B. Wurzburg, CRC Press, 1986. Specifically, Chapters 3, 8, and 10; U.S. Patent Nos. 6,190,678 and 6,200,554; and

PCT Patent Application WO 01/62376A1 assigned to Henkel.

[0061] The rinse-off products that are advantageously used with the polymer encapsulated fragrance of the present invention include laundry detergents, fabric softeners, bleaches, brighteners, personal care products such as shampoos, rinses, creams, body washes and the like. These may be liquids, solids, pastes, or gels, of any physical form.

Also included in the use of the encapsulated fragrance are applications where a second active ingredient is included to provide additional benefits for an application. The additional beneficial ingredients include fabric softening ingredients, skin moisturizers, sunscreen, insect repellent and other ingredients as may be helpful in a given application. Also included are the beneficial agents alone, that is without the fragrance.

[0062] While the preferred coating materials may be simply dissolved in water and mixed with a suspension of capsules prior to addition to the final product, other modes of coating use and application are also possible. These modes include drying the coating solution in combination with the capsule suspension for use in dry products such as detergents, or using higher concentrations of coating such that a gel structure is formed, or combining the coating material with other polymers or adjuvants which serve to improve physical characteristics or base compatibility. Drying or reducing the water content of the capsule suspension prior to coating addition is also possible, and may be preferable when using some coating materials. Further, when using some coating materials it is possible to add the coating to the application base separately from the encapsulated fragrance.

[0063] Solvents or co-solvents other than water may also be employed with the coating materials. Solvents that can be employed here are (i) polyols, such as ethylene glycol, propylene glycol, glycerol, and the like, (ii) highly polar organic solvents such as pyrrolidine, acetamide, ethylene diamine, piperazine, and the like, (iii) humectants/plasticizers for polar polymers such as monosaccharides (glucose, sucrose, etc.), amino acids, ureas and hydroxyethyl modified ureas, and the like, (iv) plasticizers for less polar polymers, such as diisodecyl adipate (DIDA), phthalate esters, and the like.

[0064] The coating polymer(s) may also be added to a suspension of capsules that contain reactive components such that the coating becomes chemically (covalently) grafted to the capsule wall, or the coating polymer(s) may be added during the crosslinking stage of the capsule wall such that covalent partial grafting of the coating takes place.

[0065] Further, if stability of the capsule and coating system is compromised by inclusion in the product base, product forms which separate the bulk of the base from the fragrance composition may be employed. The cationic coated polymer particles of the present invention may be provided in solid and liquid forms depending on the other materials to be used. In order to provide the cationic coated polymer in a dry form, it is preferable that the materials be dried using drying techniques well known in the art. In a preferred embodiment the materials are spray dried at the appropriate conditions. The spray dried particles may also be sized to provide for consistent particle size and particle size distribution. One application in which it would be advantageous to include dry particles of the present invention would be incorporated in a powdered laundry detergent. Alternatively wet capsule-coating slurries may be absorbed onto suitable dry powders to yield a flowable solid suitable for dry product use.

[0066] The present invention also includes the incorporation of a silicone or a siloxane material into a product that contains encapsulated fragrances of the present invention. As used herein silicone is meant to include both silicone and siloxane materials. Also included in the definition of silicone materials are the cationic and quaternized of the silicones. These materials are well known in the art and include both linear and branched polymers.

[0067] In addition to silicones, the present invention also includes the use of mineral oils, triglyceride oils and sucrose polyester materials in a similar matter as the silicone materials. For brevity, these materials are understood to be included in the term silicone as used in this specification unless noted to the contrary. Those with skill in the art will also appreciate that it is possible to incorporate a silicone in combination with mineral oils and the like in carrying out the present invention.

[0068] The silicone material is preferably admixed to the encapsulated fragrance-containing product after the fragrance materials are encapsulated. Optionally, the silicone material may be mixed directly with the product base either before or after the encapsulated fragrance has been added.

[0069] Suitable silicone materials include amodimethicone, polymethylalkyl siloxanes, polydimethylalkyl siloxanes, dimethicone, dimethicone copolyol, dimethiconol, disiloxane, cyclohexasiloxane, cyclomethicone, cyclopentasiloxane, phenyl dimethicone, phenyl trimethicone, silicone quaternary materials including silicone quaternium-8, and silicone quaternium-12, trimethylsiloxyamidodimethicone, trimethylsiloxysilicate and the like. These materials are commercially well known materials and are available from suppliers such as Dow Corning, Shin-Etsu, Wacker Silicones Corporation and the like. The preferred silicon is Dow Corning 245 Fluid (Dow Corning, Midland Michigan), which is described as containing greater than about 60 weight percent decamethylcyclopentasiloxane and less than or equal to about 4 weight percent dimethylcyclodisiloxanes.

[0070] Amino functional silicone oils such as those described in U.S. Patents 6,355,234 and 6,436,383 may also be used in the present invention.

[0071] Preferably the silicone materials of the present invention have a molecular weight (Mw) of from about 100 to about 200,000, preferably from about 200 to about 100,000 and most preferably from about 300 to about 50,000.

[0072] The viscosity of the silicone materials is typically from 0.5 to about 25, preferably from about 1 to about 15 and most preferably from about 2 to about 10 millimeters²sec⁻¹ using the Corporate Test Method as described in the Dow Corning product brochures.

[0073] The level of silicone used in the present invention varies by product, but is typically less than 10 percent by

weight, typically from about 0.5 to about 8 weight percent of the total weight of product. Preferably the silicon level is from about 2 to about 6 and most preferably from about 3 to about 5 weight percent of the total weight of the product.

[0074] The silicon fluid can be added to a wide array of products in order to enhance the delivery of fragrance. Suitable products include fabric conditioners and detergents, personal care products such as shampoos, liquid soap, body washes and the like; as well as in applications such as fine fragrances and colognes.

[0075] For example, a representative formulation for a fabric softener rinse product would include the following materials:

cationic quaternary ammonia softeners from about 3 to about 30 weight percent;

the encapsulated fragrance product of the present invention from about 0.1 to about 5 weight percent; and

a silicone oil from about 1 to about 10 weight percent.

[0076] The remainder of the fabric softener product may additionally contain, without limitation, brighteners, dispersibility aids, surfactants, stabilizers, soil release agents and water.

[0077] Without wishing to be bound by any theory it is believed that the silicone fluid prevents the encapsulated fragrance material from leaching from the capsule. Although the encapsulation materials are provided to prevent the loss of fragrance before usage, it is believed that the surfactants found in detergents, fabric conditioners, shampoos and other wash-off products over time leach some of the fragrance from the capsule during storage and before use. The addition of the silicone fluids to the fragrance-containing capsule materials is believed to coat the encapsulation materials with a layer of silicon that prevents the leaching of the fragrance. Another rationale for the improvement of the delivery of fragrance by the addition of silicone oils is that the oils fill vesicles in the product base. The product base such as a detergent, contains high levels of surfactant, and it is theorized that the high level of surfactant in the product bases over time removes the fragrance from the capsule. The addition of silicone to the slurry containing the encapsulated fragrance is theorized to slow the leaching of the fragrance by the surfactant, thereby providing additional and longer lasting fragrance to be delivered over time.

[0078] In another embodiment of the present invention, we have discovered that the cationic coating is not required and that the inclusion of silicon in the encapsulated mixture can provide satisfactory performance in the delivery of the fragrance. In this embodiment of the invention, the fragrance is encapsulated by the polymeric materials described above, and the level of silicon described above is provided to the encapsulated fragrance.

[0079] More specifically the present invention is directed to a composition comprising a fragrance material, said fragrance material encapsulated by a polymer to provide a polymer encapsulated fragrance, said polymer encapsulated fragrance further provided with a silicone material. This embodiment differs from other embodiments of the present invention in that the cationic polymer is not provided. The silicone oil is provided without a cationic polymer present. A description of the suitable silicone oils is provided above as well as the level of the silicon oil that is used.

[0080] The polymer encapsulated silicon material can be provided into a wide range of products, including rinse-off products including but not limited to fabric rinse conditioners, detergents, shampoos, body washes, and other cleaning products.

[0081] A preferred embodiment of the present invention is exemplified by the following formulation:

cationic quaternary ammonia softeners from about 3 to about 30 weight percent;

polymer encapsulated capsules containing fragrance from about 0.1 to about 5 weight percent; and

silicone oils from about 1 to about 10 weight percent.

[0082] The remainder of the formulation comprises water, bleaching agents, stain removers, and other ingredients known to those with skill in the art.

[0083] The mechanism of action of the present invention is not completely understood at this time. It is thought that the cationic polymer solution coats and associates with the polymeric capsules, thus imparting a positive charge which interacts with either the base or substrate in such a way as to substantially improve capsule deposition to the substrate surface.

[0084] It should be noted that the cationic character of the polymer coating used is not sufficient to determine whether it is functional with regard to improving capsule or particle deposition. Without wishing to be bound by theory, it is hypothesized that while cationic charge provides an affinity to the normally anionic substrates of interest (i.e. hair, skin, and cloth), other physical characteristics of the polymer are also important to functionality. Additionally, interactions between the capsule or particle surface, base ingredients, and the coating polymer are thought to be important to improving deposition to a given substrate.

[0085] Use of the coating systems described below allows for more efficient deposition of capsules, particles, and dispersed droplets that are coated by the cationically charged polymer. Without wishing to be bound by any theory it is believed that the advantages of the present invention is created by the combination of the cationically charged coating

which is helpful in adhering to the substrate to which the product is applied with a capsule or particle containing fragrance. Once the encapsulated particle is adhered to the substrate we have found that the encapsulated fragrance can be delivered by the fracturing or compromising of the polymer coating by actions such as brushing hair, movement of the fabric, brushing of the skin etc.

[0086] One measurement of the enhancement of the present invention in delivering the fragrance and other ingredients of the present invention is done by headspace analysis. Headspace analysis can provide a measure of the fragrance material contained on the desired substrate provided by the present invention. The present invention will provide a much higher level of fragrance on the substrate compared to the amount of fragrance deposited on the substrate by conventional means. As demonstrated by the following examples, the present invention can deliver more than about twice the level of fragrance to a substrate than common approaches, preferably more than about three times the level of fragrance and preferably more than about five times the level of fragrance than traditional approaches.

[0087] For example, this may be determined by measuring the level of fragrance imparted to a test hair swatch containing fragrance in a shampoo by conventional means as compared to the level of fragrance imparted by the present invention. The same fragrance should be used and similar test hair pieces should be washed in a similar manner. After brushing to release the fragrance from the hair, the level of fragrance on the test hair swatches of the control and the fragrance of the present invention could be measured by headspace analysis. Due to the superior adhesion of fragrance to hair by the present invention, the headspace analysis of the respective samples will demonstrate an improved level of fragrance as compared to fragrance applied by conventional means.

[0088] To better control and measure the fragrance release upon brushing or rubbing from a substrate (i.e., hair or cotton cloth), a fixed-weight of the washed and dried substrate will be placed in a custom-made glass vessel containing SILCOSTEEL (Resteck Corp., Bellefonte, PA) treated steel ball bearings. Headspace will be collected from the vessel using a Tenax trap (Supelco, Inc., Bellefonte, PA) upon equilibration. A second headspace will be collected after the substrate-containing vessel is shaken along with the steel beads on a flat bed shaker for 20 minutes. Fragrance present in the headspace from unshaken and shaken substrates and subsequently absorbed in the Tenax traps is desorbed through a Gerstel thermal desorption system (Gerstel, Inc., Baltimore, MD). Desorbed fragrance volatiles are injected into a gas chromatograph (Hewlett-Packard, Model Agilent 6890) equipped with a flame ionization detector. Area counts of individual fragrance components, identified based on the retention time, are then collected and analyzed.

[0089] These and additional modifications and improvements of the present invention may also be apparent to those with ordinary skill in the art. The particular combinations of elements described and illustrated herein are intended only to represent only a certain embodiment of the present invention and are not intended to serve as limitations of alternative articles within the spirit and scope of the invention. All materials are reported in weight percent unless noted otherwise. As used herein all percentages are understood to be weight percent.

EXAMPLE 1

Preparation of Fragrance

[0090] The following ingredients were mixed to formulate the fragrance that was used in the following examples. Unless noted to the contrary all ingredients are available from International Flavors & Fragrances Inc., N.Y., N.Y., known to those with skill in the art as IFF. P&G is understood to be Procter & Gamble Company of Cincinnati, OH.

Ingredients	Parts by weight
Ethyl-2-methyl valerate	7.143
Limonene	7.143
Dihydro myrcenol	7.143
Phenyl ethyl alcohol	7.143
Benzyl acetate	7.143
Dimeth benzyl carbonate acetate	7.143
Methyl nonyl acetaldehyde	7.143
CYCLACET (IFF)	7.143
LILIAL (Givaudan)	7.143
Hexyl salicylate	7.143

(continued)

Ingredients	Parts by weight
Tonalid	7.143
Geraniol	7.143
Methoxy naphthalene	7.143
Beta ionone	7.143

EXAMPLE 2**Preparation of Bare (Uncharged) Capsules and Cationic Polymer-Coated Capsules**

[0091] Melamine-formaldehyde capsule slurry (made by Celessence International Ltd., West Molesey, Surrey, UK) that contains approximately 32% by weight of the fragrance and 57% by weight of water was used as bare (uncharged) capsules in the following examples. To make the melamine-formaldehyde capsule slurry, a copolymer of poly acrylamide and acrylic acid was first dispersed in water together with a methylated melamine-formaldehyde resin. Fragrance was then added into the solution with high speed shearing to form small droplets. Curing of the polymeric film over the fragrance droplets as capsule wall affected by increasing the solution pH to polymerize the polymers followed by heating the solution to 50 to 85°C.

[0092] Cationic polymer-coated capsules were prepared by incorporating a mixture of cationic polymers during the curing stage of the bare capsule-making process specified above. The finished cationic capsule slurry contains 25.6% by weight of the fragrance and 56.9% by weight of water.

EXAMPLE 3**Preparation of Control Fragrance- and Bare Capsules-Containing Shampoo for Hair Swatch Washing**

[0093] The control shampoo was prepared by mixing the neat fragrance at 0.75% by weight in 30 grams of model shampoo base for 5 minutes. Shampoo that contained bare capsules without a cationic coating was prepared the same way by mixing the melamine-formaldehyde capsule slurry in shampoo to obtain 0.75% by weight fragrance. The resulting fragrance or capsules-containing shampoo was added into 570 grams of 40°C warm water and mixed for 2 minutes. Four virgin hair swatches (approximately 2.5 grams each) were added into the warm wash liquor and shaken for another 2 minutes in a 40°C water bath. Swatches were taken out from the wash liquor and rinsed sequentially in three glass jars that each contained 600 grams of clean warm water. Washing and rinsing were repeated once and excess water from hair was removed. Hair swatches were line-dried for 24 hours followed by sensory evaluation and analytical headspace analysis.

EXAMPLE 4**Preparation of Cationic Capsules-Containing Shampoo for Hair Swatch Washing**

[0094] Cationic polymer-coated capsules prepared according to Example 2 were used to mix in 30 grams of model shampoo base to obtain a fragrance level of 0.75% by weight. The resulting shampoo was used to wash four virgin hair swatches according to the procedures described in Example 3. Hair swatches were line-dried for 24 hours followed by sensory evaluation and analytical headspace analysis.

EXAMPLE 5**Sensory Evaluation and Headspace Analysis of Hair Swatches**

[0095] Dry hair swatches were evaluated by a panel of four people using the intensity scale of 0 to 5, where 0=none, 1=weak, 2=moderate, 3=strong, 4=very strong, and 5=extremely strong. Sensory scores were recorded before and after hair swatches were rubbed by hand. Deposition and release of fragrance and capsules were assessed using the purge-and-trap method followed by gas chromatography analyses on 5.0 grams of dry hair swatches before and after shaking with steel beads in enclosed vessels. Averaged sensory scores and total headspace area counts of the vari-

ables tested were reported in the following:

Hair swatch variable	Sensory score (before rubbing)	Sensory score (after rubbing)
Neat fragrance	1.7	2.0
Encapsulated fragrance without cationic polymer	2.0	2.0
Encapsulated fragrance coated with cationic polymers	3.0	3.7

CHEMICAL	Neat fragrance		Encapsulated fragrance without cationic polymer		Encapsulated fragrance with cationic polymers	
	Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
Ethyl-2-methyl valerate	278	681	117	676	2,644	7,274
Limonene	2,081	4,157	765	2,527	11,014	37,382
Dihydro myrcenol	5	61	4	99	408	3,009
Phenyl ethyl alcohol	18	67	27	225	52	168
Benzyl acetate	16	71	13	55	75	212
Geraniol	0	0	0	0	7	59
Dimethyl benzyi carbonate acetate	9	181	5	88	751	4,441
Methyl nonyl acetaldehyde	25	313	5	76	495	2,976
CYCLACET (IFF)	10	139	74	66	383	2,301
Methoxy naphthalene	21	76	9	72	174	405
Beta ionone	0	24	0	12	109	1,074
LILIAL (Givaudan)	0	25	68	117	75	691
Hexyl salicylate	0	9	3	5	15	92
Tonalid	0	0	0	0	0	12
Fragrance total area count	2,463	5,804	1,090	4,018	16,202	60,096

[0096] In this example, sensory results suggest that uncharged melamine-formaldehyde bare capsules do not to deposit on hair through shampoo washing. In addition, it is believed that friction created from rubbing was the primary key to release fragrance of deposited capsules on hair washed with cationic capsules-containing shampoo. Rubbed hair swatches washed with shampoo with cationic capsules showed appreciable sensory intensity improvement over

those washed with shampoo containing either neat fragrance or uncharged bare capsules. These observations were supported by the headspace analyses, where the headspace area counts of hair washed with cationic capsules were 10 and 15-fold over those of hair washed with neat fragrance and bare capsules after the hair was rubbed by steel beads. A significant increase of headspace area counts of hair washed with cationic capsules before rubbing also demonstrated the benefit of the cationic polymers in enhancing capsule deposition.

EXAMPLE 6

Preparation of Control Fragrance- and Capsules-Containing Powder Detergent for Fabric Swatch Washing

[0097] The control powder detergent was prepared by mixing the neat fragrance prepared in Example 1 above, at 0.3% by weight in 2.13 grams of commercially purchased powder detergent (unfragranced TIDE, Procter & Gamble). Powder detergent that contained bare capsules was prepared the same way by mixing melamine-formaldehyde capsule slurry in detergent to obtain 0.3% by weight fragrance. The resulting fragrance- or capsules-containing detergent was added into 1-liter water in a separation glass funnel. Three terry cotton swatches (approximately 2 grams each) were added into the wash liquor and shaken for 15 minutes before the wash liquor was drained from the bottom of each funnel. Excess water was removed from swatches by syringe and swatches were rinsed with 1-liter water for additional 5 minutes using the same apparatus. Rinsing was repeated once before swatches were line-dried for 24 hours followed by sensory evaluation and analytical headspace analysis.

EXAMPLE 7

Preparation of Cationic Capsules-Containing Powder Detergent for Fabric Swatch Washing

[0098] Fragrance-containing capsules with a cationic coating were prepared as described in Example 2 were used to mix in 2.13 grams of commercially purchased detergent TIDE (P&G) to obtain a fragrance level of 0.3% by weight. The resulting detergent was used to wash three fabric swatches according to the procedures described in Example 6. Fabric swatches were line-dried for 24 hours followed by sensory evaluation and analytical headspace analysis.

EXAMPLE 8

Sensory Evaluation and Headspace Analysis of Fabric Swatches Washed with Powder Detergent

[0099] Dry fabric swatches were evaluated by a panel of four people using the intensity scale of 0 to 5, where 0=none, 1=weak, 2=moderate, 3=strong, 4=very strong, and 5=extremely strong. Sensory scores were recorded before and after hair swatches were rubbed by hand. Deposition and release of fragrance and capsules were assessed using the purge-and-trap method followed by GC analyses on two dry fabric swatches before and after shaking with steel beads in enclosed vessels. Averaged sensory scores and total headspace area counts of the three variables tested were reported in the following:

Fabric swatch variable	Sensory score (before rubbing)	Sensory score (after rubbing)
Neat fragrance	1.0	0
Encapsulated fragrance without cationic polymer	0	0.8
Encapsulated fragrance coated with cationic polymers	1.5	2.5

CHEMICAL	Neat fragrance		Encapsulated fragrance without cationic polymer		Encapsulated fragrance coated with cationic polymers	
	Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
Ethyl-2-methyl valerate	0	0	0	15	31	93

(continued)

CHEMICAL	Neat fragrance		Encapsulated fragrance without cationic polymer		Encapsulated fragrance coated with cationic polymers	
	Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
Limonene	86	98	82	189	654	4,392
Dihydro myrcenol	5	10	3	14	9	12
Phenyl ethyl alcohol	740	1,258	503	845	327	761
Benzyl acetate	689	1,991	207	669	167	578
Geraniol	0	0	6	39	0	0
Dimethyl benzyl carbonate acetate	4	6	3	4	14	196
Methyl nonyl acetaldehyde	16	77	3	8	20	162
CYCLACET (IFF)	7	11	7	11	8	11
Methoxy naphthalene	0	0	0	0	0	9
Beta ionone	0	0	2	0	0	27
LILLIAL (Givaudan)	0	10	4	8	0	19
Hexyl salicylate	0	11	3	7	0	10
Tonalid	0	0	0	0	0	0
Fragrance total area count	1,547	3,472	823	1,809	1,230	6,270

[0100] Sensory results demonstrate that uncharged bare capsules slightly improved fragrance perception on rubbed cotton swatches over the neat fragrance, non-encapsulated, when used with the powder detergent. This slight intensity increase, however, was not supported by the gas chromatography headspace area counts, probably due to the low overall level of components. On the contrary, capsules coated with cationic polymers of the present invention improved sensory intensity appreciably on the swatches upon rubbing. This was confirmed analytically that 3.5 and 1.8 fold increase of headspace area counts of rubbed swatches washed with cationic capsules over those washed with bare capsules and neat fragrance.

EXAMPLE 9

Preparation and Sensory Results of Capsules-Containing Powder Detergent for Machine Washing

[0101] The control powder detergent was prepared by mixing the neat fragrance, selected as having a pleasing floral note, at 0.35% by weight in an unfragranced detergent base similar to commercially available products. Powder detergent that contained bare capsules was prepared by absorbing melamine-formaldehyde capsule slurry with Aerosil 200 (Degussa Goldschmidt Aktengesellschaft Inc.) at a 75/25 weight ratio followed by mixing it in the powder detergent to obtain 0.35% by weight fragrance. Cationic capsules-containing powder detergent was prepared in the same manner by mixing the free flow powder of Aerosil 200/cationic capsule slurry in the detergent to obtain the 0.35% by weight

fragrance. These fragrance/capsules-containing bases were also stored at 37°C/70% relative humidity condition for stability testing.

[0102] A standard set that weighted 2200 grams of towels, T-shirt, pillowcases, and tea towels was used for the Miele (Model W362) wash machine washing. A standard program of 40°C, short program, and 900 rpm spin rate was utilized. Approximately 100 milliliters of each detergent sample was used for washing experiment. Sensory ratings were obtained on dry cloths by a trained panel, panelists rubbed the towels for 1 to 2 seconds prior to smelling them, after cloths were dried in open air for a day. Initial and 2 weeks storage sensory ratings were record as follows.

Fabric towel variable	Sensory score (fresh samples)	Sensory score (Stored samples)
Neat fragrance	1.2	1.6
Encapsulated fragrance without cationic polymer	1.4	1.5
Encapsulated fragrance coated with cationic polymers	3.4	2.6

[0103] Sensory results confirmed the benefit of cationic polymers of the present invention used with capsules when incorporated in the powder detergent for large-scale machine wash. Although the sensory intensity decreased after the detergent was stored at an accelerated condition for 2 weeks, the performance of cationic capsules-containing detergent was still perceived as being far better than that of neat fragrance and bare capsules without the cationic coating.

EXAMPLE 10

Preparation of Control Fragrance- and Bare Capsules-Containing Fabric Softener for Fabric Swatch Washing

[0104] A control was prepared by mixing the neat fragrance at 1.0% by weight in 1.0 gram of liquid fabric softener. Three different fabric softener bases were used, which were commercial Downy Ultra fragrance-free fabric softener (Procter & Gamble), model fabric softeners #1 containing 9 weight % softening surfactants, and model fabric softener #2 containing 5 weight percent softening surfactant. Fabric softener that contained capsules without cationic coating was prepared the same way by mixing the melamine-formaldehyde capsule slurry in fabric softener to obtain 1.0% by weight fragrance. The resulting fragrance- or capsules-containing softener was added into 1-liter water in a separation glass funnel. Three fabric cotton swatches (approximately 2 grams each) were added into the wash liquor and stirred for 10 minutes before the wash liquor was drained from the bottom of each funnel. Excess water was removed from swatches by syringe and swatches were line-dried for 24 hours followed by sensory evaluation and analytical headspace analysis.

EXAMPLE II

Preparation of Cationic Capsules-Containing Fabric Softener for Fabric Swatch Washing

[0105] Fragrance-containing capsules coated with cationic polymers were prepared as described in Example 2 and were mixed in 1.0 gram of liquid fabric softener to obtain a fragrance level of 1.0% by weight. The resulting fabric softener was used to wash three fabric swatches according to the procedures described in Example 9. Fabric swatches were line-dried for 24 hours followed by sensory evaluation and analytical headspace analysis.

EXAMPLE 12

Sensory Evaluation and Headspace Analysis of Fabric Swatches Washed with Liquid Softener

[0106] Dry fabric swatches were evaluated by a panel of four people using the intensity scale of 0 to 5, where 0=none, 1=weak, 2=moderate, 3=strong, 4=very strong, and 5=extremely strong. Sensory scores were recorded before and after fabric swatches were rubbed by hand. Deposition and release of fragrance and capsules were assessed using the purge-and-trap method followed by GC analyses on two dry fabric swatches before and after stirring with steel beads in enclosed vessels. Averaged sensory scores and headspace area counts of the three variables tested were reported in the following:

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	Fabric swatch variable	Fabric Conditioner Base	Sensory score (before rubbing)	Sensory score (after rubbing)
5	Neat fragrance	P&G DOWNY ULTRA	1.3	1.5
	Encapsulated fragrance without cationic polymer	P&G DOWNY ULTRA	1.2	2.0
10	Encapsulated fragrance coated with cationic polymers	P&G DOWNY ULTRA	1.0	2.2
	Neat fragrance	Simulated model fabric softener product base 1	0.9	1.0
15	Encapsulated fragrance without cationic polymer	Simulated model fabric softener product base 1	2.3	3.5
	Encapsulated fragrance coated with cationic polymers	Simulated model fabric softener product base 1	2.5	4.5
20	Neat fragrance	Simulated model fabric softener product base 2	1.8	2.3
	Encapsulated fragrance without cationic polymer	Simulated model fabric softener product base 2	1.8	3.0
25	Encapsulated fragrance coated with cationic polymers	Simulated model fabric softener product base 2	2.3	4.5

30	Commercial P&G DOWNY Fabric Softener						
	CHEMICAL	Neat fragrance		Encapsulated Fragrance without Cationic Polymer		Encapsulated fragrance coated with cationic polymers	
35		Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
	Ethyl-2-methyl valerate	14	21	195	2,038	157	3,957
40	Limonene	32	63	8,456	81,512	4,291	82,294
	Dihydro myrcenol	18	122	43	683	20	759
	Phenyl ethyl alcohol	0	0	0	117	0	0
45	Benzyl acetate	71	311	147	775	127	606
	Geraniol	0	0	0	10	0	11
50	Dimethyl benzyl carbonate acetate	0	2	137	4,146	24	2,733
55	Methyl nonyl acetaldehyde	3	50	77	1,975	26	1,415

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(continued)

	Commercial P&G DOWNY Fabric Softener						
5	CHEMICAL	Neat fragrance		Encapsulated Fragrance without Cationic Polymer		Encapsulated fragrance coated with cationic polymers	
		Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
10	CYCLACET (IFF)	0	12	56	1,932	19	1,289
	Methoxy naphthalene	0	25		68	0	101
15	Beta ionone	0	4	5	600	0	457
	LILIAL (Givaudan)	0	26	3	261	0	209
	Hexyl salicylate	0	39	0	148	0	81
20	Tonalid	0	8	0	19	0	11
	Fragrance total area count	138	683	9,124	94,284	4,664	93,923
25	Simulated model fabric softener product base 1						
	CHEMICAL	Neat fragrance		Encapsulated Fragrance without Cationic Polymer		Encapsulated fragrance coated with cationic polymers	
		Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
30	Ethyl-2-methyl valerate	0	0	552	8,325	1,077	19,188
	Limonene	59	84	6,792	92,094	9,331	161,851
35	Dihydro myrcenol	41	178	11	878	81	2,533
	Phenyl ethyl alcohol	0	0	0	0	0	227
40	Benzyl acetate	29	731	38	503	486	1,983
	Geraniol	0	0	0	5	0	17
45	Dimethyl benzyl carbonate acetate	5	18	34	3,271	144	5,102
	Methyl nonyl acetaldehyde	20	115	28	2,027	90	2,740
50	CYCLACET (IFF)	0	16	12	1,580	72	2,719
	Methoxy naphthalene	0	13	4	139	15	180
55	Beta ionone	10	51	0	359	7	793

(continued)

Commercial P&G DOWNY Fabric Softener						
Simulated model fabric softener product base 1						
CHEMICAL	Neat fragrance		Encapsulated Fragrance without Cationic Polymer		Encapsulated fragrance coated with cationic polymers	
	Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
LILIAL (Givaudan)	0	28	0	208	6	353
Hexyl salicylate	0	42	0	65	0	170
Tonalid	0	10	0	10	0	18
Fragrance total area count	164	1,286	7,471	109,464	11,309	197,874

Simulated model fabric softener product base 2						
CHEMICAL	Neat fragrance		Encapsulated Fragrance without Cationic Polymer		Encapsulated fragrance coated with cationic polymers	
	Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
Ethyl-2-methyl valerate	0	0	878	8,607	796	15,925
Limonene	45	75	10,421	123,405	8,389	174,473
Dihydro myrcenol	15	41	118	1,684	37	1,978
Phenyl ethyl alcohol	0	0	0	218	0	95
Benzyl acetate	573	5,309	3,147	7,987	1,103	6,662
Geraniol	0	0	0	22	0	16
Dimethyl benzyl carbonate acetate	0	9	217	4,854	55	4,467
Methyl nonyl acetaldehyde	6	124	173	2,951	41	3,015
CYCLACET (IFF)	0	12	122	2,599	26	2,886
Methoxy naphthalene	0	8	13	119	7	173
Beta ionone	0	4	16	886	0	842
LILIAL (Givaudan)	0	34	10	456	0	468

(continued)

Simulated model fabric softener product base 2						
CHEMICAL	Neat fragrance		Encapsulated Fragrance without Cationic Polymer		Encapsulated fragrance coated with cationic polymers	
	Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
Hexyl salicylate	0	44	0	191	0	218
Tonalid	0	13	0	24	0	29
Fragrance total area count	639	5,673	15,115	154,003	10,454	211,247

[0107] Sensory results demonstrate that cationic polymers did enhance capsule deposition, thereby providing stronger sensory perception on rubbed cotton swatches, especially rinsed with simulated model fabric softener products 1 and 2 as opposed to commercially purchased DOWNY fabric softener without the cationic coated capsules. Sensory results are supported by the analytical headspace area counts in most cases.

EXAMPLE 13

Preparation and Sensory Results of Capsules-Containing Rinse Conditioners for Machine Washing

[0108] The following example employed a pleasant smelling floral fragrance added to a concentrated model fabric softener base employing a quaternary fabric softening base at a level of 1.0%, this was used as the control. Two additional samples were prepared. One by adding bare capsules containing the same fragrance and another by adding cationic capsules containing the same fragrance, both to give the equivalent of 1.0% fragrance.

[0109] A standard set that weighted 2200 grams of towels, T-shirt, pillowcases, and tea towels was used for the Miele (Model W362) wash machine washing. A standard program of 40°C, short program, and 900 rpm spin rate was utilized. Approximately 100 milliliters of a regular commercial powdered detergent was used for washing the samples and 35 ml of each of the above mentioned concentrated fabric conditioner samples were added to the conditioner drawer of the washing machines.

[0110] After line drying in the open air for 1 day sensory data was recorded. Trained panelists rubbed the cloths for 1 to 2 seconds prior to smelling them.

[0111] The cloths were then kept in an open environment for a further 14 days, they were assessed again at 7 and 14 days.

Samples in conc. TEA Quat Fab con	1 day dry	7 days dry	14 days dry
Floral control Neat oil	1.84	1.66	0.64
Floral encapsulated fragrance with cationic polymer coating	3.66	3.91	3.15
Floral encapsulated fragrance (bare)	2.63	2.62	1.84

[0112] In the above table the cationic polymer coating greatly enhances the fragrance perception from dry fabric up to and possibly beyond 14 days after washing, easily outperforming the neat oil and capsules without the coating.

Example 14

[0113] The following products were purchased at a local store for testing:

1. DOWNY ULTRA, Fabric Softener (Procter & Gamble), Free of dyes and perfumes;
2. SUAVITEL Field Flower, Fabric Softener (Colgate Palmolive Company); and
3. SNUGGLE Ultra, Pure & Gentle, (Unilever)- dye free product.

[0114] Since the above products contained varying levels of surfactant, fragrance was added proportionally to the surfactant, and the level of surfactant in the rinse water was adjusted so that the fragrance level was consistent in all the products.

[0115] A bench-top rinse procedure, followed by ambient air drying, was used to evaluate deposition on cotton cloth swatches. Analysis was conducted by evaluating the headspace by gas chromatography over the dried cloth, both without stirring and after stirring with steel balls to break the deposited capsules and release the fragrance. Cationically coated (COATED CAPSULES) similar to Example 2 described above and the encapsulated fragrance was compared against the non-encapsulated or neat fragrance.

[0116] Results are presented below:

System	Unstirred (Nanogram/ Liter)	Stirred (Nanogram/ Liter)
DOWNY ULTRA + NEAT Fragrance	17	85
DOWNY ULTRA + COATED CAPSULES	690	8674
SUAVITEL + NEAT Fragrance	62	270
SUAVITEL + COATED CAPSULES	798	10725
SNUGGLE + NEAT Fragrance	51	124
SNUGGLE + COATED CAPSULES	682	7727

[0117] As can be seen from the above results, fragrance deposition as measured by using headspace analysis was slightly better using the SUAVITEL base. This could be due to the use of different softening agents and/or surfactants or other additives present in the base. When the capsule products were stored at elevated temperature (37°C), performance declined for all the samples, although differences in stability were observed. The SUAVITEL product was most stable, the SNUGGLE product less so, and the DOWNY ULTRA product was found to be the most unstable when using the encapsulated fragrance of the present invention. Without wishing to be bound by any specific theory, the differences in the performance of the fragrance is most likely due to fragrance leaching from the capsules. The amount of fragrance leaching from the capsules is believed to be dependent on the specific surfactants used, the level of surfactants, pH and other factors in the product bases.

Claims

1. A composition comprising: a fragrance material; said fragrance material being encapsulated by a polymer to provide a polymer encapsulated fragrance; the polymer encapsulated fragrance being further coated by a polyamine polymer.
2. The composition of claim 1 wherein the polyamine product is a cationic polyamine product.
3. The composition of claim 1 or claim 2 wherein the polyamine product is a reaction product of a polyamine and an oxirane material.
4. The composition of claim 3 wherein the oxirane material is (chloromethyl) oxirane, (bromoethyl) oxirane or a mixture thereof.
5. The composition of claim 4 wherein the polymer coating comprises a reaction product of a polyamine and (chloromethyl) oxirane or (bromomethyl) oxirane and an additional cationic polymer.
6. The composition of any one of claims 1 to 5 wherein the fragrance is a liquid thereby providing a liquid core to the polymer encapsulated fragrance.
7. The fragrance of any one of claims 1 to 6 wherein the fragrance material is not water soluble.
8. The composition of any one of claims 1 to 7 wherein the fragrance material is from 10 to 50 weight percent of the composition.

9. The composition of any one of claims 1 to 8 which is incorporated into a personal care, fabric care or cleaning product.
10. The composition of claim 9 wherein the personal care product is a hair shampoo, hair rinse, bar soap or body wash.
11. A method for imparting an olfactory effective amount of fragrance into a wash-off product comprising:
- providing a fragrance material;
 - encapsulating the fragrance material with a polymer to form a polymer encapsulated fragrance;
 - providing a cationic polymer to the surface of the polymer encapsulated fragrance to form a cationically coated polymer encapsulated material; and
 - providing the coated polymer encapsulated material to a rinse off product.
12. The method of claim 11 wherein the encapsulating polymer is a vinyl polymer; an acrylate polymer, melamine-formaldehyde; urea formaldehyde or a mixture thereof.
13. A wash-off product comprising an olfactory effective amount of the composition of any one of claims 1 to 10.
14. The wash-off product of claim 13 which is a personal care, fabric care or cleaning product.
15. A wash-off product comprising the composition of any one of claims 1 to 10 and a silicone material.
16. The wash-off product of claim 15 wherein the wash-off product is a fabric rinse conditioner.
17. The wash-off product of claim 15 or claim 16 having a surfactant level of from 5 to 30 weight percent.
18. The wash-off product of any one of claims 15 to 17 having a calcium chloride level of from 0.05 to 1 weight percent.
19. The wash-off product of any one of claims 15 to 18 where the silicone level is from 0.5 to 8 weight percent of product.
20. The wash-off product of claim 19 wherein the wash-off product is a fabric rinse conditioner.
21. The wash-off product of claim 20 wherein the softening agent is provided at a level of from 10 to 20 weight percent.



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EUROPEAN SEARCH REPORT

Application Number
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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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Place of search MUNICH		Date of completion of the search 29 January 2004	Examiner Mitchell, G
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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(54) **Encapsulated fragrance chemicals**

(57) A polymeric encapsulated fragrance is disclosed which is suitable for use in personal care and cleaning products. In a preferred embodiment of the invention the fragrance is encapsulated by a first polymer

material to form a fragrance encapsulated polymer, the polymer encapsulated shell is then coated with a cationic polymer, preferably a cationic starch and guar.

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Description**Field of the Invention**

5 [0001] The present invention relates to fragrance materials that are encapsulated with a polymeric material, the encapsulated fragrance materials are further coated with a cationic polymer material. The encapsulated fragrance materials are well suited for rinse-off applications associated with personal care and cleaning products.

Background of the Invention

10 [0002] Fragrance chemicals are used in numerous products to enhance the consumer's enjoyment of a product. Fragrance chemicals are added to consumer products such as laundry detergents, fabric softeners, soaps, detergents, personal care products, such as shampoos, body washes, deodorants and the like, as well as numerous other products.

15 [0003] In order to enhance the effectiveness of the fragrance materials for the user, various technologies have been employed to enhance the delivery of the fragrance materials at the desired time. One widely used technology is encapsulation of the fragrance material in a protective coating. Frequently the protective coating is a polymeric material. The polymeric material is used to protect the fragrance material from evaporation, reaction, oxidation or otherwise dissipating prior to use. A brief overview of polymeric encapsulated fragrance materials is disclosed in the following U.S. Patents: U.S. Patent No. 4,081,384 discloses a softener or anti-stat core coated by a polycondensate suitable for use in a fabric conditioner; U.S. Patent No. 5,112,688 discloses selected fragrance materials having the proper volatility to be coated by coacervation with micro particles in a wall that can be activated for use in fabric conditioning; U.S. Patent No. 5,145,842 discloses a solid core of a fatty alcohol, ester, or other solid plus a fragrance coated by an aminoplast shell; and U.S. Patent No. 6,248,703 discloses various agents including fragrance in an aminoplast shell that is included in an extruded bar soap.

25 [0004] While encapsulation of fragrance in a polymeric shell can help prevent fragrance degradation and loss, it is often not sufficient to significantly improve fragrance performance in consumer products. Therefore, methods of aiding the deposition of encapsulated fragrances have been disclosed. U.S. Patent No. 4,234,627 discloses a liquid fragrance coated with an aminoplast shell further coated by a water insoluble meltable cationic coating in order to improve the deposition of capsules from fabric conditioners. U.S. Patent No. 6,194,375 discloses the use of hydrolyzed polyvinyl alcohol to aid deposition of fragrance-polymer particles from wash products. U.S. Patent No. 6,329,057 discloses use of materials having free hydroxy groups or pendant cationic groups to aid in the deposition of fragranced solid particles from consumer products.

30 [0005] Despite these and many other disclosures there is an ongoing need for the improved delivery of fragrance materials for various rinse-off products that provide improved performance.

Summary of the Invention

35 [0006] The present invention is directed to a polymer encapsulated fragrance, the polymer encapsulated fragrance being further treated with a cationic polymer to improve deposition.

40 [0007] More specifically the present invention is directed to a composition comprising:

a fragrance material; said fragrance material encapsulated by a polymer to create a polymer encapsulated fragrance; the polymer encapsulated fragrance being further coated by a cationic polymer. In a preferred embodiment of the invention the cationic polymer is selected from the group consisting of cationic starch and cationic guar. A method for making the cationic coated polymer encapsulated fragrances is also disclosed.

45 [0008] The present invention is well suited for use in rinse off products, which are products that are applied to a substrate and then removed in some manner. Especially preferred products that use the cationic coated polymer encapsulated fragrance of the present invention include, without limitation, hair and pet shampoos, hair conditioners, laundry detergents, fabric conditioners and the like. These and other embodiments of the present invention will become apparent upon referring to the following figure and description of the invention.

Detailed Description of the Invention

55 [0009] The fragrances suitable for use in this invention include without limitation, any combination of fragrance, essential oil, plant extract or mixture thereof that is compatible with, and capable of being encapsulated by, a polymer.

[0010] Many types of fragrances can be employed in the present invention, the only limitation being the compatibility and ability to be encapsulated by the polymer being employed, and compatibility with the encapsulation process used.

Suitable fragrances include but are not limited to fruits such as almond, apple, cherry, grape, pear, pineapple, orange, strawberry, raspberry; musk, flower scents such as lavender-like, rose-like, iris-like, and carnation-like. Other pleasant scents include herbal scents such as rosemary, thyme, and sage; and woodland scents derived from pine, spruce and other forest smells. Fragrances may also be derived from various oils, such as essential oils, or from plant materials such as peppermint, spearmint and the like. Other familiar and popular smells can also be employed such as baby powder, popcorn, pizza, cotton candy and the like in the present invention.

[0011] A list of suitable fragrances is provided in U.S. Patents 4,534,891, 5,112,688 and 5,145,842. Another source of suitable fragrances is found in Perfumes Cosmetics and Soaps, Second Edition, edited by W. A. Poucher, 1959. Among the fragrances provided in this treatise are acacia, cassie, chypre, cylamen, fern, gardenia, hawthorn, heliotrope, honeysuckle, hyacinth, jasmine, lilac, lily, magnolia, mimosa, narcissus, freshly-cut hay, orange blossom, orchids, reseda, sweet pea, trefle, tuberose, vanilla, violet, wallflower, and the like.

[0012] As used herein olfactory effective amount is understood to mean the amount of compound in perfume compositions the individual component will contribute to its particular olfactory characteristics, but the olfactory effect of the fragrance composition will be the sum of the effects of each of the fragrance ingredients. Thus the compounds of the invention can be used to alter the aroma characteristics of the perfume composition by modifying the olfactory reaction contributed by another ingredient in the composition. The amount will vary depending on many factors including other ingredients, their relative amounts and the effect that is desired.

[0013] The level of fragrance in the cationic polymer coated encapsulated fragrance varies from about 5 to about 95 weight percent, preferably from about 40 to about 95 and most preferably from about 50 to about 90 weight percent on a dry basis. In addition to the fragrance other agents can be used in conjunction with the fragrance and are understood to be included.

[0014] As noted above, the fragrance may also be combined with a variety of solvents which serve to increase the compatibility of the various materials, increase the overall hydrophobicity of the blend, influence the vapor pressure of the materials, or serve to structure the blend. Solvents performing these functions are well known in the art and include mineral oils, triglyceride oils, silicone oils, fats, waxes, fatty alcohols, and diethyl phthalate among others.

[0015] A common feature of many encapsulation processes is that they require the fragrance material to be encapsulated to be dispersed in aqueous solutions of polymers, pre-condensates, surfactants, and the like prior to formation of the capsule walls. Therefore, materials having low solubility in water, such as highly hydrophobic materials are preferred, as they will tend to remain in the dispersed perfume phase and partition only slightly into the aqueous solution. Fragrance materials with Clog P values greater than 1, preferably greater than 3, and most preferably greater than 5 will thus result in microcapsules that contain cores most similar to the original composition, and will have less possibility of reacting with materials that form the capsule shell.

[0016] One object of the present invention is to deposit capsules containing fragrance cores on desired substrates such as cloth, hair, and skin during washing and rinsing processes. Further, it is desired that, once deposited, the capsules release the encapsulated fragrance either by diffusion through the capsule wall, via small cracks or imperfections in the capsule wall caused by drying, physical, or mechanical means, or by large-scale rupture of the capsule wall. In each of these cases, the volatility of the encapsulated perfume materials is critical to both the speed and duration of release, which in turn control consumer perception. Thus, fragrance chemicals which have higher volatility as evidenced by normal boiling points of less than 250°C, preferably less than about 225°C are preferred in cases where quick release and impact of fragrance is desired. Conversely, fragrance chemicals that have lower volatility (boiling points greater than 225°C) are preferred when a longer duration of aroma is desired. Of course, fragrance chemicals having varying volatility may be combined in any proportions to achieve the desired speed and duration of perception.

[0017] In order to provide the highest fragrance impact from the fragrance encapsulated capsules deposited on the various substrates referenced above, it is preferred that materials with a high odor-activity be used. Materials with high odor-activity can be detected by sensory receptors at low concentrations in air, thus providing high fragrance perception from low levels of deposited capsules. This property must be balanced with the volatility as described above. Some of the principles mentioned above are disclosed in U.S. Patent No. 5,112,688.

[0018] Further, it is clear that materials other than fragrances may be employed in the system described here. Examples of other materials which may be usefully deposited from rinse-off products using the invention include sunscreens, softening agents, insect repellents, and fabric conditioners, among others.

[0019] Encapsulation of fragrances is known in the art, see for example U.S. Patent Nos. 2,800,457, 3,870,542, 3,516,941, 3,415,758, 3,041,288, 5,112,688, 6,329,057, and 6,261,483. Another discussion of fragrance encapsulation is found in the Kirk-Othmer Encyclopedia.

[0020] Preferred encapsulating polymers include those formed from melamine-formaldehyde or urea-formaldehyde condensates, as well as similar types of aminoplasts. Additionally, capsules made via the simple or complex coacervation of gelatin are also preferred for use with the coating. Capsules having shell walls comprised of polyurethane, polyamide, polyolefin, polysaccharide, protein, silicone, lipid, modified cellulose, gums, polyacrylate, polyphosphate, polystyrene, and polyesters or combinations of these materials are also functional.

[0021] A representative process used for aminoplast encapsulation is disclosed in U.S. Patent No. 3,516,941 though it is recognized that many variations with regard to materials and process steps are possible. A representative process used for gelatin encapsulation is disclosed in U.S. Patent No. 2,800,457 though it is recognized that many variations with regard to materials and process steps are possible. Both of these processes are discussed in the context of

france encapsulation for use in consumer products in U.S. Patent Nos. 4,145,184 and 5,112,688 respectively.

[0022] Well known materials such as solvents, surfactants, emulsifiers, and the like can be used in addition to the polymers described above to encapsulate the fragrance without departing from the scope of the present invention. It is understood that the term encapsulated is meant to mean that the fragrance material is substantially covered in its entirety. Encapsulation can provide pore vacancies or interstitial openings depending on the encapsulation techniques employed. More preferably the entire fragrance material portion of the present invention is encapsulated.

[0023] Particles comprised of fragrance and a variety of polymeric and non-polymeric matrixing materials are also suitable for use. These may be composed of polymers such as polyethylene, fats, waxes, or a variety of other suitable materials. Essentially any capsule, particle, or dispersed droplet may be used that is reasonably stable in the application and release of fragrance at an appropriate time once deposited.

[0024] Particle and capsule diameter can vary from about 10 nanometers to about 1000 microns, preferably from about 50 nanometers to about 100 microns and is most preferably from about 2 to about 15 microns. The capsule distribution can be narrow, broad, or multimodal. Multi-modal distributions may be composed of different types of capsule chemistries.

[0025] Once the fragrance material is encapsulated a cationically charged water-soluble polymer is applied to the fragrance encapsulated polymer. This water-soluble polymer can also be an amphoteric polymer with a ratio of cationic and anionic functionalities resulting in a net total charge of zero and positive, i.e., cationic. Those skilled in the art would appreciate that the charge of these polymers can be adjusted by changing the pH, depending on the product in which this technology is to be used. Any suitable method for coating the cationically charged materials onto the encapsulated fragrance materials can be used. The nature of suitable cationically charged polymers for assisted capsule delivery to interfaces depends on the compatibility with the capsule wall chemistry since there has to be some association to the capsule wall. This association can be through physical interactions, such as hydrogen bonding, ionic interactions, hydrophobic interactions, electron transfer interactions or, alternatively, the polymer coating could be chemically (covalently) grafted to the capsule or particle surface. Chemical modification of the capsule or particle surface is another way to optimize anchoring of the polymer coating to capsule or particle surface. Furthermore, the capsule and the polymer need to want to go to the desired interface and, therefore, need to be compatible with the chemistry (polarity, for instance) of that interface. Therefore, depending on which capsule chemistry and interface (e.g., cotton, polyester, hair, skin, wool) is used the cationic polymer can be selected from one or more polymers with an overall zero (amphoteric: mixture of cationic and anionic functional groups) or net positive charge, based on the following polymer backbones: polysaccharides, polypeptides, polycarbonates, polyesters, polyolefinic (vinyl, acrylic, acrylamide, poly diene), polyester, polyether, polyurethane, polyoxazoline, polyamine, silicone, polyphosphazine, polyaromatic, poly heterocyclic, or polyionene, with molecular weight (MW) ranging from about 1,000 to about 1000,000,000, preferably from about 5,000 to about 10,000,000. As used herein molecular weight is provided as weight average molecular weight. Optionally, these cationic polymers can be used in combination with nonionic and anionic polymers and surfactants, possibly through coacervate formation.

[0026] A more detailed list of cationic polymers that can be used to coat the encapsulated fragrance is provided below:

[0027] Polysaccharides include but are not limited to guar, alginates, starch, xanthan, chitosan, cellulose, dextrans, arabic gum, carrageenan, hyaluronates. These polysaccharides can be employed with:

(a) cationic modification and alkoxy-cationic modifications, such as cationic hydroxyethyl, cationic hydroxy propyl.

For example, cationic reagents of choice are 3-chloro-2-hydroxypropyl trimethylammonium chloride or its epoxy version. Another example is graft-copolymers of polyDADMAC on cellulose like in Celquat L-200 (Polyquaternium-4), Polyquaternium-10 and Polyquaternium-24, commercially available from National Starch, Bridgewater, N.J.;

(b) aldehyde, carboxyl, succinate, acetate, alkyl, amide, sulfonate, ethoxy, propoxy, butoxy, and combinations of these functionalities. Any combination of Amylose and Amylopectin and overall molecular weight of the polysaccharide; and

(c) any hydrophobic modification (compared to the polarity of the polysaccharide backbone).

[0028] The above modifications described in (a), (b) and (c) can be in any ratio and the degree of functionalization up to complete substitution of all functionalizable groups, and as long as the theoretical net charge of the polymer is zero (mixture of cationic and anionic functional groups) or preferably positive. Furthermore, up to 5 different types of functional groups may be attached to the polysaccharides. Also, polymer graft chains may be differently modified than the backbone. The counterions can be any halide ion or organic counter ion. U.S. Patent Nos. 6,297,203 and U.S. 6,200,554.

[0029] Another source of cationic polymers contain protonatable amine groups so that the overall net charge is zero (amphoteric: mixture of cationic and anionic functional groups) or positive. The pH during use will determine the overall net charge of the polymer. Examples are silk protein, zein, gelatin, keratin, collagen and any polypeptide, such as polylysine.

[0030] Further cationic polymers include poly vinyl polymers, with up to 5 different types of monomers, having the monomer generic formula $-C(R_2)(R_1)-CR_2R_3-$. Any co-monomer from the types listed in this specification may also be used. The overall polymer will have a net theoretical positive charge or equal to zero (mixture of cationic and anionic functional groups). Where R1 is any alkanes from C1-C25 or H; the number of double bonds ranges from 0-5. Furthermore, R1 can be an alkoxyated fatty alcohol with any alkoxy carbon-length, number of alkoxy groups and C1-C25 alkyl chain length. R1 can also be a liquid crystalline moiety that can render the polymer thermotropic liquid crystalline properties, or the alkanes selected can result in side-chain melting. In the above formula R2 is H or CH3; and R3 is -C1, -NH2, -NHR1, -NR1R2, -NR1R2R6 (where R6 = R1, R2, or -CH2-COOH or its salt), -NH-C(O)-H, -C(O)-NH2 (amide), -C(O)-N(R2)(R2')(R2''), -OH, styrene sulfonate, pyridine, pyridine-N-oxide, quaternized pyridine, imidazolium halide, imidazolium halide, imidazol, piperidine, pyrrolidone, alkyl-substituted pyrrolidone, caprolactam or pyridine, phenyl-R4 or naphthalene-R5 where R4 and R5 are R1, R2, R3, sulfonic acid or its alkali salt -COOH, -COO- alkali salt, ethoxy sulphate or any other organic counter ion. Any mixture of these R3 groups may be used. Further suitable cationic polymers containing hydroxy alkyl vinyl amine units, as disclosed in U.S. Patent No 6,057,404.

[0031] Another class of materials are polyacrylates, with up to 5 different types of monomers, having the monomer generic formula: $-CH(R_1)-C(R_2)(CO-R_3-R_4)-$. Any co-monomer from the types listed in this specification may also be used. The overall polymer will have a net theoretical positive charge or equal to zero (mixture of cationic and anionic functional groups). In the above formula R1 is any alkane from C1-C25 or H with number of double bonds from 0-5, aromatic moieties, polysiloxane, or mixtures thereof. Furthermore, R1 can be an alkoxyated fatty alcohol with any alkoxy carbon-length, number of alkoxy groups and C1-C25 alkyl chain length. R1 can also be a liquid crystalline moiety that can render the polymer thermotropic liquid crystalline properties, or the alkanes selected can result in side-chain melting. R2 is H or CH3; R3 is alkyl alcohol C1-25 or an alkylene oxide with any number of double bonds, or R3 may be absent such that the C=O bond is (via the C-atom) directly connected to R4. R4 can be: -NH2, NHR1, -NR1R2, -NR1R2R6 (where R6 = R1, R2, or -CH2-COOH or its salt), -NH-C(O)-, sulfo betaine, betaine, polyethylene oxide, poly(ethyleneoxide/propylene oxide/butylene oxide) grafts with any end group, H, OH, styrene sulfonate, pyridine, quaternized pyridine, alkyl-substituted pyrrolidone or pyridine, pyridine-N-oxide, imidazolium halide, imidazolium halide, imidazol, piperidine, -OR1, -OH, -COOH alkali salt, sulfonate, ethoxy sulphate, pyrrolidone, caprolactam, phenyl-R4 or naphthalene-R5 where R4 and R5 are R1, R2, R3, sulfonic acid or its alkali salt or organic counter ion. Any mixture of these R3 groups may be used. Also, glyoxylated cationic polyacrylamides can be used. Typical polymers of choice are those containing the cationic monomer dimethylaminoethyl methacrylate (DMAEMA) or methacrylamidopropyl trimethyl ammonium chloride (MAPTAC). DMAEMA can be found in Gafquat and Gaffix VC-713 polymers from ISP. MAPTAC can be found in BASF's Luviquat PQ11 PN and ISP's Gafquat HS100.

[0032] Another group of polymers that can be used are those that contain cationic groups in the main chain or backbone. Included in this group are:

(1) polyalkylene imines such as polyethylene imine, commercially available as Lupasol from BASF. Any molecular weight and any degree of crosslinking of this polymer can be used in the present invention;

(2) ionenes having the general formula set forth as

$-[N(+)(R_1R_2-A_1-N(R_5)-X-N(R_6)-A_2-N(+)(R_3R_4-A_3)]_n-2Z-$, as disclosed in U.S. Patent Nos. 4,395,541 and U.S. 4,597,962;

(3) adipic acid/dimethyl amino hydroxypropyl diethylene triamine copolymers, such as Cartaretin F-4 and F-23, commercially available from Sandoz;

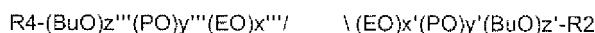
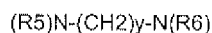
(4) polymers of the general formula $-N(CH_3)_2-(CH_2)_x-NH-(CO)-NH-(CH_2)_y-N(CH_3)_2-(CH_2)_z-O-(CH_2)_p]_n-$, with x, y, z, p=1-12, and n according to the molecular weight requirements. Examples are Polyquaternium 2 (Mirapol A-15), Polyquaternium-17 (Mirapol AD-1), and Polyquaternium-18 (Mirapol AZ-1).

[0033] Other polymers include cationic polysiloxanes and cationic polysiloxanes with carbon-based grafts with a net theoretical positive charge or equal to zero (mixture of cationic and anionic functional groups). This includes cationic end-group functionalized silicones (i.e. Polyquaternium-80). Silicones with general structure: $-[Si(R_1)(R_2)-O]_x-[Si(R_3)(R_2)-O]_y-$ where R1 is any alkane from C1-C25 or H with number of double bonds from 0-5, aromatic moieties, polysiloxane grafts, or mixtures thereof. R1 can also be a liquid crystalline moiety that can render the polymer thermotropic liquid crystalline properties, or the alkanes selected can result in side-chain melting. R2 can be H or CH3 and R3 can be -R1-R4, where R4 can be -NH2, -NHR1, -NR1R2, -NR1R2R6 (where R6 = R1, R2, or -CH2-COOH or its salt), -NH-C(O)-, -COOH, -COO- alkali salt, any C1-25 alcohol, -C(O)-NH2 (amide), -C(O)-N(R2)(R2')(R2''), sulfo betaine, betaine, polyethylene oxide, poly(ethyleneoxide/propylene oxide/butylene oxide) grafts with any end group,

H, -OH, styrene sulfonate, pyridine, quaternized pyridine, alkyl-substituted pyrrolidone or pyridine, pyridine-N-oxide, imidazolium halide, imidazolium halide, imidazol, piperidine, pyrrolidone, caprolactam, -COOH, -COO⁻ alkali salt, sulfonate, ethoxy sulphate phenyl-R5 or naphthalene-R6 where R5 and R6 are R1, R2, R3, sulfonic acid or its alkali salt or organic counter ion. R3 can also be -(CH₂)_x-O-CH₂-CH(OH)-CH₂-N(CH₃)₂-CH₂-COOH and its salts. Any mixture of these R3 groups can be selected. X and y can be varied as long as the theoretical net charge of the polymer is zero (amphoteric) or positive. In addition, polysiloxanes containing up to 5 different types of monomeric units may be used. Examples of suitable polysiloxanes are found in U.S. Patent Nos. 4,395,541 4,597,962 and U.S.6,200,554. Another group of polymers that can be used to improve capsule/particle deposition are phospholipids that are modified with cationic polysiloxanes. Examples of these polymers are found in U.S. Patent No. 5,849,313, WO Patent Application 9518096A1 and European Patent EP0737183B1.

[0034] Furthermore, copolymers of silicones and polysaccharides and proteins can be used (Crodasone Series).

[0035] Another class of polymers include polyethylene oxide-co-propyleneoxide-co-butylene oxide polymers of any ethylene oxide/propylene oxide / butylene oxide ratio with cationic groups resulting in a net theoretical positive charge or equal to zero (amphoteric). The general structure is:



where R1,2,3,4 is -NH₂, -N(R)3- X⁺, R with R being H or any alkyl group. R5,6 is -CH₃ or H. Counter ions can be any halide ion or organic counter ion. X, Y, may be any integer, any distribution with an average and a standard deviation and all 12 can be different. Examples of such polymers are the commercially available TETRONIC brand polymers.

[0036] Suitable polyheterocyclic (the different molecules appearing in the backbone) polymers include the piperazine-alkylene main chain copolymers disclosed in Ind. Eng. Chem. Fundam., (1986), 25, pp.120-125, by Isamu Kashiki and Akira Suzuki.

[0037] Also suitable for use in the present invention are copolymers containing monomers with cationic charge in the primary polymer chain. Up to 5 different types of monomers may be used. Any co-monomer from the types listed in this specification may also be used. Examples of such polymers are poly diallyl dimethyl ammonium halides (Poly-DADMAC) copolymers of DADMAC with vinyl pyrrolidone, acrylamides, imidazoles, imidazolium halides, etc. These polymers are disclosed in Henkel EP0327927A2 and PCT Patent Application 01/62376A1. Also suitable are Poly-quaternium-6 (Merquat 100), Polyquaternium-7 (Merquats S, 550, and 2200), Polyquaternium-22 (Merquats 280 and 295) and Polyquaternium-39 (Merquat Plus 3330), available from Ondeo Nalco.

[0038] Polymers containing non-nitrogen cationic monomers of the general type -CH₂-C(R1)(R2-R3-R4)- can be used with: R1 being a -H or C1-C20 hydrocarbon. R2 is a disubstituted benzene ring or an ester, ether, or amide linkage. R3 is a C1-C20 hydrocarbon, preferably C1-C10, more preferably C1-C4. R4 can be a trialkyl phosphonium, dialkyl sulfonium, or a benzopyrilium group, each with a halide counter ion. Alkyl groups for R4 are C1-C20 hydrocarbon, most preferably methyl and t-butyl. These monomers can be copolymerized with up to 5 different types of monomers. Any co-monomer from the types listed in this specification may also be used.

[0039] Substantivity of these polymers may be further improved through formulation with cationic, amphoteric and nonionic surfactants and emulsifiers, or by coacervate formation between surfactants and polymers or between different polymers. Combinations of polymeric systems (including those mentioned previously) may be used for this purpose as well as those disclosed in EP1995/000400185.

[0040] Furthermore, polymerization of the monomers listed above into a block, graft or star (with various arms) polymers can often increase the substantivity toward various surfaces. The monomers in the various blocks, graft and arms can be selected from the various polymer classes listed in this specification.

[0041] The preferred cationically charged materials are selected from the group consisting of cationically modified starch and cationically modified guar, polymers comprising poly diallyl dimethyl ammonium halides (PolyDADMAC), and copolymers of DADMAC with vinyl pyrrolidone, acrylamides, imidazoles, imidazolium halides, and the like. For instance, Polyquaternium-6, 7, 22 and 39, all available from Ondeo Nalco.

[0042] The preferred cationic starch has a molecular weight of from about 100,000 to about 500,000,000, preferably from about 200,000 to about 10,000,000 and most preferably from about 250,000 to about 5,000,000. The preferred cationic starch products are HI-CAT CWS42 and HI-CAT 02 and are commercially available from ROQUETTE AMERICA, Inc.

[0043] The preferred cationic guar has a molecular weight of from about 50,000 to about 5,000,000. The preferred cationic guar products are Jaguar C-162 and Jaguar C-17 and are commercially available from Rhodia Inc.

[0044] The level of cationic polymer is from about 1% to about 3000%, preferably from about 5% to about 1000% and most preferably from about 10% to about 500% of the fragrance containing compositions, based on a ratio with the fragrance on a dry basis.

[0045] The weight ratio of the encapsulating polymer to fragrance is from about 1:25 to about 1:1. Preferred products have had the weight ratio of the encapsulating polymer to fragrance varying from about 1:10 to about 4:96.

[0046] For example, if a capsule blend has 20 weight % fragrance and 20 weight % polymer, the polymer ratio would be (20/20) multiplied by 100 (%) = 100%.

[0047] The present invention, the encapsulated fragrance is well suited for wash-off products. Wash-off products are understood to be those products that are applied for a given period of time and then are removed. These products are common in areas such as laundry products, and include detergents, fabric conditioners, and the like; as well as personal care products which include shampoos, hair rinses, body washes, soaps and the like.

[0048] We have discovered that the present invention is advantageously applied to products, including fabric rinse conditioners, having a pH of less than 7, preferably less than about 5 and most preferably less than about 4.

[0049] A better product, including wash-off products such as fabric rinse conditioner is also obtained when the salt level is limited. The improvement in the fabric rinse conditioner is noted by a longer lasting and/or improved delivery of fragrance. One method of improving the delivery of the encapsulated fragrance is to limit the amount of salt in the product base. Preferably the level of salt in the rinse conditioner product is less than or equal to about 1 weight percent by weight in the product, preferably less than about 0.5 weight percent and most preferably less than about 0.1 weight percent.

[0050] More specifically we have discovered that limiting the level of calcium chloride will improve the delivery of the fragrance using the encapsulated fragrance of the present invention. Improved fragrance delivery is provided by limiting the amount of calcium chloride to less than about 2 weight percent, typically less than 1 weight percent and more preferably less than 0.5 weight percent. As is known in the art, calcium chloride is added to control viscosity of the formulations, so there is trade-off between the viscosity and fragrance delivery. We have discovered suitable formulations with calcium chloride levels of from about 0.05 to about 1 weight percent of the formulation, preferably from about 0.1 to about 0.7 and most preferably from about 0.25 to about 0.5 weight percent of the formulation. We have discovered that limiting the level of calcium chloride level as set forth above is particularly advantageous in fabric rinse conditioner products.

[0051] Another means for improving the performance of delivery of the encapsulated fragrance of the present invention is to limit the level of some softening agents. We have discovered that limiting the softening actives, such as triethanolamine quaternary, diethanolamine quaternary, ACCOSOFT cationic surfactants (Stepan Chemical), or dital-low dimethyl ammonium chloride (DTDMAC), to an amount of from about 5 to about 30 weight percent of the product, preferably from about 10 to about 20 and more preferably from about 12 to 14 weight percent of a fabric rinse conditioner product will improve the performance of the fragrance. The above softening agents are well known in the art and are disclosed in U.S. Patents 6,521,589 and 6,180,594.

[0052] Yet another means for improving fragrance delivery of the present invention is to limit the level of the non-ionic surfactants employed in the product, including a fabric softening product. Many non-ionic surfactants are known in the art and include alkyl ethoxylate, commercially available as NEODOL (Shell Oil Company), nonyl phenol ethoxylate, TWEEN surfactants (ICI Americas Inc.), and the like. We have discovered that the encapsulated fragrance of the present invention are advantageously used when the non-ionic surfactant level is below about 5 weight percent of the product, preferably less than about 1 weight percent and most preferably less than 0.5 weight percent.

[0053] Yet another means for enhancing the fabric softener product is to limit the level of co-solvent included in the fabric softener in addition to water. Reducing the level of co solvents such as ethanol and isopropanol to less than about 5 weight percent of the product, preferably less than about 2 and most preferably less than about 1 weight percent of the fabric softener product has been found to improve fragrance delivery.

[0054] Improved fragrance performance includes longer lasting fragrance, improved substantivity of the fragrance on cloth or the ability to provide improved fragrance notes, such as specific fragrance notes through the use of the present invention.

[0055] While the above description is primarily to fabric rinse conditioner products, additional studies for shampoos, detergent and other cleaning products have also led to preferred embodiments for these products as well.

[0056] As was found for fabric rinse conditioners, additional studies have determined that lower pH is desirable for the delivery of fragrance when used in the product base. The preferred bases are neutral or mildly acidic, preferably having a pH of 7, more preferably less than about 5 and most preferably less than about 4 for shampoos, detergent and other cleaning products.

[0057] We have found that powder detergent and other cleaning products provide enhanced fragrance delivery when the material coating the encapsulating polymer is also neutral or slightly acidic. Preferred materials are NaHSO₄, acetic

acid, citric acid and other similar acidic materials and their mixtures. These materials have a pH of less than about 7, preferably less than about 5 and most preferably less than about 4.

[0058] As was described with fabric rinse conditioners, lower surfactant levels were advantageously employed in shampoos, detergents and other cleaning products bases with the present invention. The level of surfactant is preferably less than about 30, more preferably less than about 20 and most preferably less than about 10 weight percent of the product base. A similar finding was found with preferred levels of salt in shampoos, detergents and other cleaning products as was found in fabric rinse conditioners. The salt level is preferably less than about 5 weight percent, more preferably less than about 2 and most preferably less than 0.5 weight percent of the product.

[0059] Lower solvent levels found in the base improves the fragrance delivery in shampoos, detergents and other cleaning products as well. Solvents, include but are not limited to, ethanol, isopropanol, dipropylene glycol in addition to the water base and the hydrotope level is preferably less than 5 weight percent, preferably less than about 2 and most preferably less than 1 weight percent of the total product base.

[0060] A preferred surfactant base for shampoos, detergents and other cleaning products was found to be ethoxylated surfactants such as alkyl ethoxylated sulfates, $(C_{12}-C_{14})(\text{ethylene oxide})_n\text{SO}_4\text{M}$; or ethoxylated carboxylate surfactants $(C_{12}-C_{14})(\text{Ethylene oxide})_n\text{COOM}$ where n is from 1 to about 15 and M is Na^+ , K^+ or NH_4^+ cation. A more preferred class of surfactants for use in the present invention was zwitterionic surfactants such as the alkyl amine oxides, taurides, betaines and sulfobetaines. Zwitterionic surfactants are disclosed in greater detail in U.S. Patent 6,569,826. Other commercially available surfactants are AMPHOSOL series of betaines (Stepan Chemical); TEGO-TIAN by Goldschmidt; and HOSTAPAN and ARKOPAN by Clariant

[0061] The most preferred surfactant system to be employed with the encapsulated fragrance system of the present invention was found to be non-ionic surfactants. Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_8-C_{20} aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the $C_{10}-C_{15}$ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide). These nonionic surfactants are disclosed in U.S. Patent 6,517,588.

[0062] Polymers that are known as deposition aids, and in a preferred embodiment are also cationic can be found in the following resources:

Encyclopedia of Polymers and Thickeners for Cosmetics, Robert Lochhead and William From, in Cosmetics & Toiletries, Vol. 108, May 1993, pp. 95-138;
 Modified Starches: Properties & Uses, O. B. Wurzburg, CRC Press, 1986. Specifically, Chapters 3, 8, and 10;
 U.S. Patent Nos. 6,190,678 and 6,200,554; and
 PCT Patent Application WO 01/62376A1 assigned to Henkel.

[0063] The rinse-off products that are advantageously used with the polymer encapsulated fragrance of the present invention include laundry detergents, fabric softeners, bleaches, brighteners, personal care products such as shampoos, rinses, creams, body washes and the like. These may be liquids, solids, pastes, or gels, of any physical form. Also included in the use of the encapsulated fragrance are applications where a second active ingredient is included to provide additional benefits for an application. The additional beneficial ingredients include fabric softening ingredients, skin moisturizers, sunscreen, insect repellent and other ingredients as may be helpful in a given application. Also included are the beneficial agents alone, that is without the fragrance.

[0064] While the preferred coating materials may be simply dissolved in water and mixed with a suspension of capsules prior to addition to the final product, other modes of coating use and application are also possible. These modes include drying the coating solution in combination with the capsule suspension for use in dry products such as detergents, or using higher concentrations of coating such that a gel structure is formed, or combining the coating material with other polymers or adjuvants which serve to improve physical characteristics or base compatibility. Drying or reducing the water content of the capsule suspension prior to coating addition is also possible, and may be preferable when using some coating materials. Further, when using some coating materials it is possible to add the coating to the application base separately from the encapsulated fragrance.

[0065] Solvents or co-solvents other than water may also be employed with the coating materials. Solvents that can be employed here are (i) polyols, such as ethylene glycol, propylene glycol, glycerol, and the like, (ii) highly polar organic solvents such as pyrrolidine, acetamide, ethylene diamine, piperazine, and the like, (iii) humectants/plasticizers for polar polymers such as monosaccharides (glucose, sucrose, etc.), amino acids, ureas and hydroxyethyl modified ureas, and the like, (iv) plasticizers for less polar polymers, such as diisodecyl adipate (DIDA), phthalate esters, and the like.

[0066] The coating polymer(s) may also be added to a suspension of capsules that contain reactive components such that the coating becomes chemically (covalently) grafted to the capsule wall, or the coating polymer(s) may be

added during the crosslinking stage of the capsule wall such that covalent partial grafting of the coating takes place.

[0067] The present invention also includes the incorporation of a silicone or a siloxane material into a product that contains encapsulated fragrances of the present invention. As used herein silicone is meant to include both silicone and siloxane materials. Also included in the definition of silicone materials are the cationic and quaternized of the silicones. These materials are well known in the art and include both linear and branched polymers.

[0068] In addition to silicones, the present invention also includes the use of mineral oils, triglyceride oils and sucrose polyester materials in a similar matter as the silicone materials. For brevity, these materials are understood to be included in the term silicone as used in this specification unless noted to the contrary. Those with skill in the art will also appreciate that it is possible to incorporate a silicone in combination with mineral oils and the like in carrying out the present invention.

[0069] The silicone material is preferably admixed to the encapsulated fragrance-containing product after the fragrance materials are encapsulated. Optionally, the silicone material may be mixed directly with the product base either before or after the encapsulated fragrance has been added.

[0070] Suitable silicone materials include amodimethicone, polymethylalkyl siloxanes, polydimethylalkyl siloxanes, dimethicone, dimethicone copolyol, dimethiconol, disiloxane, cyclohexasiloxane, cyclomethicone, cyclopentasiloxane, phenyl dimethicone, phenyl trimethicone, silicone quaternary materials including silicone quaternium-8, and silicone quaternium-12, trimethylsiloxyamidodimethicone, trimethylsiloxysilicate and the like. These materials are commercially well known materials and are available from suppliers such as Dow Corning, Shin-Etsu, Wacker Silicones Corporation and the like. The preferred silicon is Dow Corning 245 Fluid (Dow Corning, Midland Michigan), which is described as containing greater than about 60 weight percent decamethylcyclopentasiloxane and less than or equal to about 4 weight percent dimethylcyclasiloxanes.

[0071] Amino functional silicone oils such as those described in U.S. Patents 6,355,234 and 6,436,383 may also be used in the present invention.

[0072] Preferably the silicone materials of the present invention have a molecular weight (Mw) of from about 100 to about 200,000, preferably from about 200 to about 100,000 and most preferably from about 300 to about 50,000.

[0073] The viscosity of the silicone materials is typically from 0.5 to about 25, preferably from about 1 to about 15 and most preferably from about 2 to about 10 millimeters²sec⁻¹ using the Corporate Test Method as described in the Dow Corning product brochures.

[0074] The level of silicone used in the present invention varies by product, but is typically less than 10 percent by weight, typically from about 0.5 to about 8 weight percent of the total weight of product. Preferably the silicon level is from about 2 to about 6 and most preferably from about 3 to about 5 weight percent of the total weight of the product.

[0075] The silicon fluid can be added to a wide array of products in order to enhance the delivery of fragrance. Suitable products include fabric conditioners and detergents, personal care products such as shampoos, liquid soap, body washes and the like; as well as in applications such as fine fragrances and colognes.

[0076] For example, a representative formulation for a fabric softener rinse product would include the following materials:

cationic quaternary ammonia softeners from about 3 to about 30 weight percent;
the encapsulated fragrance product of the present invention from about 0.1 to about 5 weight percent; and
a silicone oil from about 1 to about 10 weight percent.

[0077] The remainder of the fabric softener product may additionally contain, without limitation, brighteners, dispersibility aids, surfactants, stabilizers, soil release agents and water.

[0078] Without wishing to be bound by any theory it is believed that the silicone fluid prevents the encapsulated fragrance material from leaching from the capsule. Although the encapsulation materials are provided to prevent the loss of fragrance before usage, it is believed that the surfactants found in detergents, fabric conditioners, shampoos and other wash-off products over time leach some of the fragrance from the capsule during storage and before use. The addition of the silicone fluids to the fragrance-containing capsule materials is believed to coat the encapsulation materials with a layer of silicon that prevents the leaching of the fragrance. Another rationale for the improvement of the delivery of fragrance by the addition of silicone oils is that the oils fill vesicles in the product base. The product base such as a detergent, contains high levels of surfactant, and it is theorized that the high level of surfactant in the product bases over time removes the fragrance from the capsule. The addition of silicone to the slurry containing the encapsulated fragrance is theorized to slow the leaching of the fragrance by the surfactant, thereby providing additional and longer lasting fragrance to be delivered over time.

[0079] In another embodiment of the present invention, we have discovered that the cationic coating is not required and that the inclusion of silicon in the encapsulated mixture can provide satisfactory performance in the delivery of the fragrance. In this embodiment of the invention, the fragrance is encapsulated by the polymeric materials described above, and the level of silicon described above is provided to the encapsulated fragrance.

[0080] More specifically the present invention is directed to a composition comprising a fragrance material, said fragrance material encapsulated by a polymer to provide a polymer encapsulated fragrance, said polymer encapsulated fragrance further provided with a silicone material. This embodiment differs from other embodiments of the present invention in that the cationic polymer is not provided. The silicone oil is provided without a cationic polymer present. A description of the suitable silicone oils is provided above as well as the level of the silicon oil that is used.

[0081] The polymer encapsulated silicon material can be provided into a wide range of products, including rinse-off products including but not limited to fabric rinse conditioners, detergents, shampoos, body washes, and other cleaning products.

[0082] A preferred embodiment of the present invention is exemplified by the following formulation:

cationic quaternary ammonia softeners from about 3 to about 30 weight percent;
polymer encapsulated capsules containing fragrance from about 0.1 to about 5 weight percent; and
silicone oils from about 1 to about 10 weight percent.

[0083] The remainder of the formulation comprises water, bleaching agents, stain removers, and other ingredients known to those with skill in the art.

[0084] Further, if stability of the capsule and coating system is compromised by inclusion in the product base, product forms which separate the bulk of the base from the fragrance composition may be employed. The cationic coated polymer particles of the present invention may be provided in solid and liquid forms depending on the other materials to be used. In order to provide the cationic coated polymer in a dry form, it is preferable that the materials be dried using drying techniques well known in the art. In a preferred embodiment the materials are spray dried at the appropriate conditions. The spray dried particles may also be sized to provide for consistent particle size and particle size distribution. One application in which it would be advantageous to include dry particles of the present invention would be incorporated in a powdered laundry detergent. Alternatively wet capsule-coating slurries may be absorbed onto suitable dry powders to yield a flowable solid suitable for dry product use.

[0085] The mechanism of action of the present invention is not completely understood at this time. It is thought that the cationic polymer solution coats and associates with the polymeric capsules, thus imparting a positive charge which interacts with either the base or substrate in such a way as to substantially improve capsule deposition to the substrate surface.

[0086] It should be noted that the cationic character of the polymer coating used is not sufficient to determine whether it is functional with regard to improving capsule or particle deposition. Without wishing to be bound by theory, it is hypothesized that while cationic charge provides an affinity to the normally anionic substrates of interest (i.e. hair, skin, and cloth), other physical characteristics of the polymer are also important to functionality. Additionally, interactions between the capsule or particle surface, base ingredients, and the coating polymer are thought to be important to improving deposition to a given substrate.

[0087] Use of the coating systems described below allows for more efficient deposition of capsules, particles, and dispersed droplets that are coated by the cationically charged polymer. Without wishing to be bound by any theory it is believed that the advantages of the present invention is created by the combination of the cationically charged coating which is helpful in adhering to the substrate to which the product is applied with a capsule or particle containing fragrance. Once the encapsulated particle is adhered to the substrate we have found that the encapsulated fragrance can be delivered by the fracturing or compromising of the polymer coating by actions such as brushing hair, movement of the fabric, brushing of the skin etc.

[0088] One measurement of the enhancement of the present invention in delivering the fragrance and other ingredients of the present invention is done by headspace analysis. Headspace analysis can provide a measure of the fragrance material contained on the desired substrate provided by the present invention. The present invention will provide a much higher level of fragrance on the substrate compared to the amount of fragrance deposited on the substrate by conventional means. As demonstrated by the following examples, the present invention can deliver more than about twice the level of fragrance to a substrate than common approaches, preferably more than about three times the level of fragrance and preferably more than about five times the level of fragrance than traditional approaches.

[0089] For example, this may be determined by measuring the level of fragrance imparted to a test hair swatch containing fragrance in a shampoo by conventional means as compared to the level of fragrance imparted by the present invention. The same fragrance should be used and similar test hair pieces should be washed in a similar manner. After brushing to release the fragrance from the hair, the level of fragrance on the test hair swatches of the control and the fragrance of the present invention could be measured by headspace analysis. Due to the superior adhesion of fragrance to hair by the present invention, the headspace analysis of the respective samples will demonstrate an improved level of fragrance as compared to fragrance applied by conventional means.

[0090] To better control and measure the fragrance release upon brushing or rubbing from a substrate (i.e., hair or cotton cloth), a fixed-weight of the washed and dried substrate will be placed in a custom-made glass vessel containing

SILCOSTEEL (Resteck Corp., Bellefont, PA) treated steel ball bearings. Headspace will be collected from the vessel using a Tenax trap (Supelco, Inc., Bellefonte, PA) upon equilibration. A second headspace will be collected after the substrate-containing vessel is shaken along with the steel beads on a flat bed shaker for 20 minutes. Fragrance present in the headspace from unshaken and shaken substrates and subsequently absorbed in the Tenax traps is desorbed through a Gerstel thermal desorption system (Gerstel, Inc., Baltimore, MD). Desorbed fragrance volatiles are injected into a gas chromatograph (Hewlett-Packard, Model Agilent 6890) equipped with a flame ionization detector. Area counts of individual fragrance components, identified based on the retention time, are then collected and analyzed.

[0091] These and additional modifications and improvements of the present invention may also be apparent to those with ordinary skill in the art. The particular combinations of elements described and illustrated herein are intended only to represent only a certain embodiment of the present invention and are not intended to serve as limitations of alternative articles within the spirit and scope of the invention. All materials are reported in weight percent unless noted otherwise. As used herein all percentages are understood to be weight percent.

EXAMPLE 1

Preparation of Fragrance

[0092] The following ingredients were mixed to formulate the fragrance that was used in the following examples. Unless noted to the contrary all ingredients are available from International Flavors & Fragrances Inc., N.Y., N.Y., known to those with skill in the art as IFF. P&G is understood to be Procter & Gamble Company of Cincinnati, OH.

Ingredients	Parts by weight
Ethyl-2-methyl valerate	7.143
Limonene	7.143
Dihydro myrcenol	7.143
Phenyl ethyl alcohol	7.143
Benzyl acetate	7.143
Dimethyl benzyl carbonate acetate	7.143
Methyl nonyl acetaldehyde	7.143
CYCLACET (IFF)	7.143
LILIAL (Givaudan)	7.143
Hexyl salicylate	7.143
Tonalid	7.143
Geraniol	7.143
Methoxy naphthalene	7.143
Beta ionone	7.143

EXAMPLE 2

Preparation of Cationic Polymer-Coated Capsules

[0093] Individual polymer solutions were prepared by mixing selected cationic polymers at 5% by weight in 50°C warm water until fully dissolved under constant stirring. Cationic polymers used in this example are the following: cationic starch (HI-CAT CWS42 from Roquette America Inc.), cationic guar (Jaguar C-162 from Rhodia Inc.), Luviquat (HM550 and PQ11-PN from BASF Aktengesellschaft Inc.), Abil Quat (3474 from Degussa Goldschmidt Chemical Corp.), and Cel Quat (L-200 from National Starch Inc.).

[0094] Cationic polymer-coated capsules were prepared by mixing uncoated fragrance-containing capsules and the polymer solution specified above at the level of desire. In this example, melamine-formaldehyde capsule slurry (uncoated capsules made by Cellescence International Ltd., West Molesey, Surrey, UK) that contains approximately 32% by weight of the fragrance and 57% by weight of water was used. To make the capsule slurry, a copolymer of poly

acrylamide and acrylic acid was first dispersed in water together with a methylated melamine-formaldehyde resin. Fragrance was then added into the solution with high speed shearing to form small droplets. Curing of the polymeric film over the fragrance droplets as capsule wall effected by increasing the solution pH to polymerize the polymers followed by heating the solution to 50 to 85°C. To prepare cationic capsule slurry that contains cationic polymers at 63% by weight of the fragrance, 2.84 grams of the polymer solution was mixed with 0.7 grams of the capsule slurry until homogeneous.

[0095] Three different cationic capsule slurries were prepared using cationic starch (HI-CAT CWS42) at 10%, 30%, and 63% by weight of the fragrance. In the same manner, three additional cationic capsule slurries were prepared using cationic guar (Jaguar C-162) at 63%, 120%, and 300% by weight of the fragrance. Other polymers (Luviquat, Abil Quat, and Cel Quat) were used at 63% by weight of the fragrance.

EXAMPLE 3

Preparation of Control Fragrance- and Bare Capsules-Containing Shampoo for Hair Swatch Washing

[0096] The control shampoo was prepared by mixing the neat fragrance at 0.75% by weight in 30 grams of model shampoo base for 5 minutes. Shampoo that contained bare capsules without a cationic coating was prepared the same way by mixing the melamine-formaldehyde capsule slurry in shampoo to obtain 0.75% by weight fragrance. The resulting fragrance- or capsules-containing shampoo was added into 570 grams of 40°C warm water and mixed for 2 minutes. Four virgin hair swatches (approximately 2.5 grams each) were added into the warm wash liquor and shaken for another 2 minutes in a 40°C water bath. Swatches were taken out from the wash liquor and rinsed sequentially in three glass jars that each contained 600 grams of clean warm water. Washing and rinsing were repeated once and excess water from hair was removed. Hair swatches were line-dried for 24 hours followed by sensory evaluation and analytical headspace analysis.

EXAMPLE 4

Preparation of Cationic Capsules-Containing Shampoo for Hair Swatch Washing

[0097] Cationic polymer-coated capsules prepared according to Example 2 were used to mix in 30 grams of model shampoo base to obtain a fragrance level of 0.75% by weight. The resulting shampoo was used to wash four virgin hair swatches according to the procedures described in Example 3. Hair swatches were line-dried for 24 hours followed by sensory evaluation and analytical headspace analysis.

EXAMPLE 5

Sensory Evaluation and Headspace Analysis of Hair Swatches

[0098] Dry hair swatches were evaluated by a panel of four people using the intensity scale of 0 to 5, where 0=none, 1=weak, 2=moderate, 3=strong, 4=very strong, and 5=extremely strong. Sensory scores were recorded before and after hair swatches were rubbed by hand. Deposition and release of fragrance and capsules were assessed using the purge-and-trap method followed by GC analyses on 5.0 grams of dry hair swatches before and after shaking with steel beads in enclosed vessels. Averaged sensory scores and total headspace area counts of the variables tested were reported in the following:

Hair Swatch Variable	Sensory Score (Before Rubbing)	Sensory Score (After Rubbing)
Neat fragrance	1.7	2.0
Encapsulated fragrance without cationic polymer	2.0	2.0
Encapsulated fragrance coated with cationic starch (63% fragrance)	3.3	5.0
Encapsulated fragrance coated with cationic starch (30% fragrance)	3.7	5.0

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(continued)

Hair Swatch Variable	Sensory Score (Before Rubbing)	Sensory Score (After Rubbing)
Encapsulated fragrance coated with cationic starch (10% fragrance)	3.0	4.7
Encapsulated fragrance coated with cationic guar (300% fragrance)	4.0	5.0
Encapsulated fragrance coated with cationic guar (120% fragrance)	2.3	4.7
Encapsulated fragrance coated with cationic guar (63% fragrance)	2.3	2.3
Encapsulated fragrance coated with Luviquat HM552/PQ11-PN (63% fragrance)	1.3	1.6
Encapsulated fragrance coated with Abil Quat 3474 (63% fragrance)	1.3	1.6
Encapsulated fragrance coated with Cel Quat L-200(63% fragrance)	1.3	1.3

Chemical	Neat Fragrance		Encapsulated Fragrance Without Cationic Polymer	
	Unshaken	Shaken	Unshaken	Shaken
Ethyl-2-methyl valerate	278	681	117	676
Limonene	2,081	4,157	765	2,527
Dihydro myrcenol	5	61	4	99
Phenyl ethyl alcohol	18	67	27	225
Benzyl acetate	16	71	13	55
Geraniol	0	0	0	0
Dimethyl benzyl carbonate acetate	9	181	5	88
Methyl nonyl acetaldehyde	25	313	5	76
CYCLACET (IFF)	10	139	74	66
Methoxy naphthalene	21	76	9	72
Beta ionone	0	24	0	12
LILIAL (Givaudan)	0	25	68	117
Hexyl salicylate	0	9	3	5
Tonalid	0	0	0	0
Fragrance Total Area Count	2,463	5,804	1,090	4,018

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Chemical	Encapsulated Fragrance Coated with Cationic starch (63% Fragrance)		Encapsulated Fragrance Coated with Cationic Starch (30% Fragrance)		Encapsulated Fragrance Coated with Cationic Starch (10% Fragrance)	
	Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
Ethyl-2-methyl valerate	1,253	27,877	998	23,570	1,071	26,914
Limonene	10,585	195,482	9,111	193,141	3,130	63,419
Dihydro myrcenol	292	20,634	92	11,864	198	12,282
Phenyl ethyl alcohol	67	333	21	165	32	164
Benzyl acetate	0	146	9	135	6	78
Geraniol	0	123	0	40	0	70
Dimethyl benzyl carbonate acetate	385	14,408	141	10,420	112	5,393
Methyl nonyl acetaldehyde	256	12,308	122	8,583	54	2,857
CYCLACET (IFF)	177	9,180	89	6,167	56	2,804
Methoxy naphthalene	41	831	21	492	20	506
Beta ionone	32	4,161	14	2,889	7	920
LILIAL (Givaudan)	27	2,517	10	1,743	4	509
Hexyl salicylate	9	412	3	304	0	63
Tonalid	0	33	0	27	0	7
Fragrance Total Area Count	13,124	288,445	10,631	259,540	4,690	115,986

Chemical	Encapsulated Fragrance Coated with Cationic Guar (300% Fragrance)		Encapsulated Fragrance Coated with Cationic Guar (120% Fragrance)		Encapsulated Fragrance Coated with Cationic Guar (63% Fragrance)	
	Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
Ethyl-2-methyl valerate	2,573	29,873	868	15,973	243	2,726
Limonene	11,164	123,014	5,095	129,185	1,636	27,218
Dihydro myrcenol	380	10,903	142	10,319	24	1,675

(continued)

Chemical	Encapsulated Fragrance Coated with Cationic Guar (300% Fragrance)		Encapsulated Fragrance Coated with Cationic Guar (120% Fragrance)		Encapsulated Fragrance Coated with Cationic Guar (63% Fragrance)	
	Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
Phenyl ethyl alcohol	31	97	46	188	53	239
Benzyl acetate	60	373	15	105	0	60
Geraniol	9	272	0	126	0	8
Dimethyl benzyl carbonate acetate	459	6,874	113	7,118	18	2,959
Methyl nonyl acetaldehyde	358	6,760	82	5,753	18	2,108
CYCLACET (IFF)	241	5,011	57	4,263	16	1,209
Methoxy naphthalene	141	906	27	482	0	119
Beta ionone	44	2,459	12	2,171	6	421
LILIAL (Givaudan)	31	1,424	9	1,365	2	347
Hexyl salicylate	4	236	0	208	0	49
Tonalid	0	22	0	16	0	7
Fragrance Total Area Count	15,495	188,224	6,466	177,272	2,016	39,145

[0099] These results demonstrated that the following: cationic starch and cationic guar were both superior to the other cationic polymers tested, a cationic starch was far more effective than cationic guar on a same weight basis in enhancing capsule deposition on hair. Data also showed that capsule deposition was dependent on the concentration of cationic polymers present in the capsule slurry. At the highest polymer concentration of cationic starch tested (63% of fragrance), headspace area counts suggested a total fragrance deposition was improved approximately 50-fold over the neat fragrance, i.e., non-encapsulated fragrance. Headspace area counts of cationic guar at 300% and 120% of fragrance was found between those of cationic starch at 30% and 10% of fragrance, although sensory scores are very close to each other which can be explained by dose-response relationship.

[0100] The averaged nitrogen to carbon ratio (by weight) of tested cationic polymers was determined as the following: 0.022, 0.0061, 0.041, 0.29, and 0.17 for Jaguar C-162, HI-CAT CWS42, Cel Quat L-200, Luviquat HM552, and Luviquat PQ11-PN, respectively. It is evident that the cationic starch used in this example did not possess the highest cationic charge density, yet best performance was obtained through the enhanced capsule deposition on hair.

EXAMPLE 6

Preparation of Control Fragrance- and Bare Capsules-Containing Powder Detergent for Fabric Swatch Washing

[0101] The control powder detergent was prepared by mixing the neat fragrance prepared in Example 1 above, at 0.3% by weight in 2.13 grams of commercial powder detergent (unfragranced TIDE, Procter & Gamble). Powder detergent that contained capsules without the cationic coating was prepared the same way by mixing melamine-formaldehyde capsule slurry in detergent to obtain 0.3% by weight fragrance. The resulting fragrance- or capsules-containing

detergent was added into 1-liter water in a separation glass funnel. Three terry cotton swatches (approximately 2 grams each) were added into the wash liquor and shaken for 15 minutes before the wash liquor was drained from the bottom of each funnel. Excess water was removed from swatches by syringe and swatches were rinsed with 1-liter water for additional 5 minutes using the same apparatus. Rinsing was repeated once before swatches were line-dried for 24 hours followed by sensory evaluation and analytical headspace analysis.

EXAMPLE 7

Preparation of Cationic Capsules-Containing Powder Detergent for Fabric Swatch Washing

[0102] Fragrance-containing capsules with a cationic coating were prepared as described in Example 2 were used to mix in 2.13 grams of commercial powder TIDE to obtain a fragrance level of 0.3% by weight. The resulting detergent was used to wash three fabric swatches according to the procedures described in Example 6. Fabric swatches were line-dried for 24 hours followed by sensory evaluation and analytical headspace analysis.

EXAMPLE 8

Sensory Evaluation and Headspace Analysis of Fabric Swatches Washed with Powder Detergent

[0103] Dry fabric swatches were evaluated by a panel of four people using the intensity scale of 0 to 5, where 0=none, 1=weak, 2=moderate, 3=strong, 4=very strong, and 5=extremely strong. Sensory scores were recorded before and after hair swatches were rubbed by hand. Deposition and release of fragrance and capsules were assessed using the purge-and-trap method followed by gas chromatography analyses on two dry fabric swatches before and after shaking with steel beads in enclosed vessels. Averaged sensory scores and total headspace area counts of the three variables tested were reported in the following:

Fabric Swatch Variable	Sensory Score (Before Rubbing)	Sensory Score (After Rubbing)
Neat fragrance	1.0	0.0
Encapsulated fragrance without cationic polymer	0.0	1.8
Cationic starch-coated capsules (polymer at 100% fragrance)	1.5	3.3

Chemical	Neat Fragrance		Encapsulated Fragrance Without Cationic Polymer		Encapsulated Fragrance Coated With Cationic Starch (100% Fragrance)	
	Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
Ethyl-2-methyl valerate	0	0	0	15	19	88
Limonene	86	98	82	189	3,343	57,411
Dihydro myrcenol	5	10	3	14	24	19
Phenyl ethyl alcohol	740	1,258	503	845	685	1,557
Benzyl acetate	689	1,991	207	669	298	1,304
Geraniol	0	0	6	39	0	8
Dimethyl benzyl carbonate acetate	4	6	3	4	47	2,224
Methyl nonyl acetaldehyde	16	77	3	8	35	1,542
CYCLACET (IFF)	7	11	7	11	8	14
Methoxy naphthalene	0	0	0	0	0	21
Beta ionone	0	0	2	0	0	357
LILLIAL (Givaudan)	0	10	4	8	4	235
Hexyl salicylate	0	11	3	7	4	9
Tonalid	0	0	0	0	0	14
Fragrance Total Area Count	1,547	3,472	823	1,809	4,467	64,803

[0104] Sensory results showed that encapsulated fragrance materials slightly improved fragrance perception over the neat fragrance, non-encapsulated, when used with the powder detergent. This slight intensity increase, however, was not supported by the gas chromatography headspace area counts, probably due to the low overall level of components. The use of cationic starch significantly improved the fragrance deposition on cotton swatches over both bare capsules and neat fragrance. These observations were fully supported by the headspace area counts above swatches, both before and after stirred with steel beads.

EXAMPLE 9

Preparation of Control Fragrance- and Bare Capsules-Containing Fabric Softener for Fabric Swatch Washing

[0105] A control was prepared by mixing the neat fragrance at 1.0% by weight in 1.0 gram of liquid fabric softener. Four different fabric softener bases were used, which were commercial Downy fragrance-free fabric softener (Procter & Gamble), model fabric softeners #1 containing 9 weight % softening surfactants, model fabric softener #2 containing

13 weight percent softening surfactant, and model fabric softener #3 containing 5 weight % softening surfactant. Fabric softener that contained capsules without cationic coating was prepared the same way by mixing the melamine-formaldehyde capsule slurry in fabric softener to obtain 1.0% by weight fragrance. The resulting fragrance- or capsules-containing softener was added into 1-liter water in a separation glass funnel. Three fabric cotton swatches (approximately 2 grams each) were added into the wash liquor and stirred for 10 minutes before the wash liquor was drained from the bottom of each funnel. Excess water was removed from swatches by syringe and swatches were line-dried for 24 hours followed by sensory evaluation and analytical headspace analysis.

EXAMPLE 10

Preparation of Cationic Capsules-Containing Fabric Softener for Fabric Swatch Washing

[0106] Fragrance-containing capsules coated with cationic starch were prepared as described in Example 2 and were mixed in 1.0 gram of liquid fabric softener to obtain a fragrance level of 1.0% by weight. The resulting fabric softener was used to wash three fabric swatches according to the procedures described in Example 9. Fabric swatches were line-dried for 24 hours followed by sensory evaluation and analytical headspace analysis.

EXAMPLE 11

Sensory Evaluation and Headspace Analysis of Fabric Swatches Washed With Liquid Softener

[0107] Dry fabric swatches were evaluated by a panel of four people using the intensity scale of 0 to 5, where 0=none, 1=weak, 2=moderate, 3=strong, 4=very strong, and 5=extremely strong. Sensory scores were recorded before and after fabric swatches were rubbed by hand. Deposition and release of fragrance and capsules were assessed using the purge-and-trap method followed by GC analyses on two dry fabric swatches before and after stirring with steel beads in enclosed vessels. Averaged sensory scores and headspace area counts of the three variables tested were reported in the following:

Fabric Swatch Variable	Fabric Conditioner Base	Sensory Score (Before Rubbing)	Sensory Score (After Rubbing)
Neat fragrance	P&G DOWNY ULTRA	1.3	1.5
Encapsulated fragrance without cationic polymer	P&G DOWNY ULTRA	1.2	2.0
Encapsulated fragrance coated with cationic starch (100% fragrance)	P&G DOWNY ULTRA	1.2	2.2
Neat fragrance	Simulated model fabric softener product base 1	0.9	1.0
Encapsulated fragrance without cationic polymer	Simulated model fabric softener product base 1	2.3	3.5
Encapsulated fragrance coated with cationic starch (100% fragrance)	Simulated model fabric softener product base 1	3.2	4.8
Neat fragrance	Simulated model fabric softener product base 2	1.3	1.3
Encapsulated fragrance without cationic polymer	Simulated model fabric softener product base 2	1.8	3.2
Encapsulated fragrance coated with cationic starch (100% fragrance)	Simulated model fabric softener product base 2	2.2	3.8
Neat fragrance	Simulated model fabric softener product base 3	1.8	2.3

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Fabric Swatch Variable	Fabric Conditioner Base	Sensory Score (Before Rubbing)	Sensory Score (After Rubbing)
Encapsulated fragrance without cationic polymer	Simulated model fabric softener product base	1.8	3.0
Encapsulated fragrance coated with cationic starch (100% fragrance)	Simulated model fabric softener product base 3	2.5	4.5

Commercial P&G DOWNY Fabric Softener						
Chemical	Neat Fragrance		Encapsulated Fragrance Without Cationic Polymer		Encapsulated Fragrance Coated With Cationic Starch (100% Fragrance)	
	Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
Ethyl-2-methyl valerate	14	21	195	2,038	452	2,935
Limonene	32	63	8,456	81,512	15,907	91,289
Dihydro myrcenol	18	122	43	683	70	885
Phenyl ethyl alcohol	0	0	0	117	33	127
Benzyl acetate	71	311	147	775	282	697
Geraniol	0	0	0	10	0	19
Dimethyl benzyl carbonate acetate	0	2	137	4,146	243	3,470
Methyl nonyl acetaldehyde	3	50	77	1,975	181	2,044
CYCLACET (IFF)	0	12	56	1,932	132	1,847
Methoxy naphthalene	0	25	5	68	10	70
Beta ionone	0	4	5	600	23	527
LILIAL (Givaudan)	0	26	3	261	26	236
Hexyl salicylate	0	39	0	148	7	103
Tonalid	0	8	0	19	0	10
Fragrance Total Area Count	138	683	9,124	94,284	17,366	104,259

SIMULATED MODEL FABRIC SOFTENER PRODUCT BASE 1						
Chemical	Neat Fragrance		Encapsulated Fragrance Without Cationic Polymer		Encapsulated Fragrance Coated With Cationic Starch (100% Fragrance)	
	Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
Ethyl-2-methyl valerate	0	0	552	8,325	2,354	27,508
Limonene	59	84	6,792	92,094	16,087	182,103
Dihydro myrcenol	41	178	11	878	67	3,764
Phenyl ethyl alcohol	0	0	0	0	0	141
Benzyl acetate	29	731	38	503	221	1,382
Geraniol	0	0	0	5	0	6
Dimethyl benzyl carbonate acetate	5	18	34	3,271	91	6,684
Methyl nonyl acetaldehyde	20	115	28	2,027	86	4,283
CYCLACET (IFF)	0	16	12	1,580	49	3,732
Methoxy naphthalene	0	13	4	139	23	329
Beta ionone	10	51	0	359	4	1,215
LILIAL (Givaudan)	0	28	0	208	3	617
Hexyl salicylate	0	42	0	65	0	216
Tonalid	0	10	0	10	0	22
Fragrance Total Area Count	164	1,286	7,471	109,464	18,985	232,002

SIMULATED MODEL FABRIC SOFTENER PRODUCT BASE 2						
Chemical	Neat Fragrance		Encapsulated Fragrance Without Cationic Polymer		Encapsulated Fragrance Coated With Cationic Starch (100% Fragrance)	
	Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
Ethyl-2-methyl valerate	0	0	478	7,345	510	9,360
Limonene	61	78	10,762	151,790	9,775	177,293
Dihydro myrcenol	33	52	22	1,766	29	2,017

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SIMULATED MODEL FABRIC SOFTENER PRODUCT BASE 2						
Chemical	Neat Fragrance		Encapsulated Fragrance Without Cationic Polymer		Encapsulated Fragrance Coated With Cationic Starch (100% Fragrance)	
	Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
Phenyl ethyl alcohol	0	0	7	90	43	101
Benzyl acetate	342	1,696	208	2,627	725	5,019
Geraniol	0	3	0	13	0	15
Dimethyl benzyl carbonate acetate	4	12	29	5,987	40	6,347
Methyl nonyl acetaldehyde	19	119	35	4,024	34	3,277
CYCLACET (IFF)	13	28	20	3,314	24	3,430
Methoxy naphthalene	0	25	0	149	4	115
Beta ionone	19	53	2	1,107	0	994
LILIAL (Givaudan)	51	454	0	608	0	425
Hexyl salicylate	0	75	0	263	0	200
Tonalid	0	21	0	37	0	21
Fragrance Total Area Count	542	2,612	11,563	179,120	11,184	208,614

SIMULATED MODEL FABRIC SOFTENER PRODUCT BASE 3						
Chemical	Neat Fragrance		Encapsulated Fragrance Without Cationic Polymer		Encapsulated Fragrance Coated With Cationic Starch (100% Fragrance)	
	Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
Ethyl-2-methyl valerate	0	0	878	8,607	1,307	25,601
Limonene	45	75	10,421	123,405	19,858	330,854
Dihydro myrcenol	15	41	118	1,684	47	4,431
Phenyl ethyl alcohol	0	0	0	218	9	249
Benzyl acetate	573	5,309	3,147	7,987	127	1,070
Geraniol	0	0	0	22	0	27

(continued)

SIMULATED MODEL FABRIC SOFTENER PRODUCT BASE 3						
Chemical	Neat Fragrance		Encapsulated Fragrance Without Cationic Polymer		Encapsulated Fragrance Coated With Cationic Starch (100% Fragrance)	
	Unshaken	Shaken	Unshaken	Shaken	Unshaken	Shaken
Dimethyl benzyl carbonate acetate	0	9	217	4,854	102	10,430
Methyl nonyl acetaldehyde	6	124	173	2,951	105	7,410
CYCLACET (IFF)	0	12	122	2,599	52	6,724
Methoxy naphthalene	0	8	13	119	7	304
Beta ionone	0	4	16	886	4	2,301
LILIAL (Givaudan)	0	34	10	456	3	1,215
Hexyl salicylate	0	44	0	191	0	518
Tonalid	0	13	0	24	0	68
Fragrance Total Area Count	639	5,673	15,115	154,003	21,621	391,202

[0108] Sensory data indicated that cationic starch improved capsule deposition in all tested rinse conditioners. Simulated model fabric softener product base 1 and simulated model fabric softener product base 2 were two bases that yielded the highest benefit, suggesting the specific base composition is a factor that influences deposition and the magnitude of perceived sensory. Analytical headspace area counts confirmed this observation.

Claims

1. A composition comprising: a fragrance material; said fragrance material being encapsulated by a polymer to provide a polymer encapsulated fragrance; the polymer encapsulated fragrance being further coated by a cationic polymer.
2. The composition of claim 1 wherein the fragrance is a liquid thereby providing a liquid core to the polymer encapsulated fragrance.
3. The fragrance of claim 1 or claim 2 wherein the fragrance material is not water soluble.
4. The composition of any one of claims 1 to 3 wherein the fragrance material is from 10 to 50 weight percent of the composition.
5. The composition of any one of claims 1 to 4 which is incorporated into a personal care, fabric care or cleaning product.
6. The composition of claim 5 wherein the personal care product is a hair shampoo, hair rinse, bar soap or body wash.
7. A method for imparting an olfactory effective amount of fragrance into a wash-off product comprising:

providing a fragrance material;
 encapsulating the fragrance material with a polymer to form a polymer encapsulated fragrance;
 providing a cationic polymer to the surface of the polymer encapsulated fragrance to form a cationically coated
 polymer encapsulated material; and
 providing the cationically coated polymer encapsulated material to a rinse off product.

8. The method of claim 7 wherein the encapsulating polymer is a vinyl polymer; an acrylate polymer, melamine-formaldehyde; urea formaldehyde or a mixture thereof.

9. The method of claim 7 or claim 8 wherein the cationic polymer is a polysaccharide, a cationically modified starch, a cationically modified guar, a polysiloxane, a polydiallyl dimethyl ammonium halide, a copolymer of polydiallyl dimethyl ammonium chloride and vinyl pyrrolidone, an acrylamide, an imidazole, an imidazolium halide or an imidazolium halide.

10. The method of claim 9 wherein the cationic polymer is a cationically modified starch or a cationically modified guar.

11. A wash-off product comprising an olfactory effective amount of the composition of any one of claims 1 to 6.

12. The wash-off product of claim 11 which is a personal care, fabric care or cleaning product.

13. A wash-off product comprising the composition of any one of Claims 1 to 6 and a silicone material.

14. The wash-off product of claim 13 wherein the wash-off product is a fabric rinse conditioner.

15. The wash-off product of claim 14 having a surfactant level of from 5 to 30 weight percent.

16. The wash-off product of claim 14 or claim 15 having a calcium chloride level of from 0.05 to 1 weight percent.

17. The wash-off product of any one of claims 13 to 16 wherein the silicone level is from 0.5 to 8 weight percent.

18. The wash-off product of claim 17 which is a fabric rinse conditioner.

19. The wash-off product of claim 20 wherein the softening agent is provided at a level of from 10 to 20 weight percent.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 03 25 6378

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Place of search MUNICH		Date of completion of the search 29 January 2004	Examiner Mitchell, G
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US91/00905 (22) International Filing Date: 11 February 1991 (11.02.91) (30) Priority data: 482,441 20 February 1990 (20.02.90) US (71) Applicants: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Ctr. - Bldg. 220-12W-01, St. Paul, MN 55144 (US). (72) Inventors: WALLEY, Darlene, Rose ; 9576 Carriage Run Circle, Loveland, OH 45140 (US). BUTTERY, Howard, John ; 1240 Kolff Curt, Newport, MN 55055 (US). NORBURY, Robert, James ; 3724 Gershwin Avenue, Oakdale, MN 55128 (US). SCHMIDT, Diane, Grob ; 9902 Hunters Run Lane, Cincinnati, OH 45242 (US). MICHAEL, William, Robert ; 7432 Pinebrook Drive, Cincinnati, OH 45224 (US).		(74) Agents: REED, T., David et al.; The Procter & Gamble Company, Ivorydale Technical Ctr., 5299 Spring Grove Ave., Cincinnati, OH 45217-1087 (US). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, PL, SE (European patent), SU. Published <i>With international search report.</i>
(54) Title: COATED PERFUME PARTICLES (57) Abstract <p>Perfume particles comprise perfume dispersed within certain water-insoluble nonpolymeric carrier materials and encapsulated in a protective shell by coating with a friable coating material. The coated particles allow for preservation and protection of perfumes which are susceptible to degradation or loss in storage and in cleaning compositions. In use, the surface coating fractures and the underlying carrier/perfume particles efficiently deliver a large variety of perfume types to fabrics or other surfaces.</p>		

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COATED PERFUME PARTICLES

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Technical Field

The present invention relates to perfume particles which comprise perfume dispersed within a relatively low molecular weight nonpolymeric carrier material, and encapsulated with a friable coating. Such coated particles are useful, for example, in cleaning and fabric conditioning compositions.

Background of the Invention

This invention is based on the concept of controlled perfume release, i.e., perfume release at a time and under conditions that will achieve the desired perfume effect. In general, this is a very old idea, and various methods for achieving this end have been developed, from the simple idea of putting perfume in wax candles to the complex technology of microencapsulation.

One aspect of the concept of controlled release of perfume is providing slow release of perfume over an extended period of time. This is generally achieved by blending perfume with a substance that will, in essence, "trap" the perfume so that small amounts of perfume are released over time. The use of high molecular weight polymeric substances having perfume incorporated therein to provide controlled release of perfume over time is known. See, for example, U.S. Patent 4,184,099 Lindauer et al, issued January 15, 1980; European Patent Application 0 028 118, Leonard, published May 6, 1981; and U.S. Patent 4,110,261, Newland, issued August 29, 1978, which teach combining perfume with a release controlling medium and forming the combination into a solid product for air freshening.

Textile laundering is also concerned with controlled release of perfumes. Application of this concept allows for slowing down or preventing release of perfume through long periods of shelf storage. Such a concept also allows for using much lower levels of perfume in product since much less perfume is wasted.

Perfume preservation over storage times can be achieved in a variety of ways. The perfume can be made a part of the package for the composition. The perfume can be combined with plastic

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used to make a bottle, or the perfume can be mixed with a polymer substance and the product used to coat a cardboard package composition, as is disclosed in U.S. Patent 4,540,721, Staller, issued September 10, 1985. Either way the perfume is released over time from the polymer matrix.

The perfume/controlled release agent may also be in the form of particles mixed into the laundry composition. One method taught to achieve this end is combining the perfume with a water-soluble polymer, forming into particles and adding to a laundry composition, as is described in U.S. Patent 4,209,417, Whyte, issued June 24, 1980; U.S. Patent 4,339,356, Whyte, issued July 13, 1982; and U.S. Patent 3,576,760, Gould et al, issued April 27, 1971.

The perfume may also be adsorbed onto a porous carrier material, which may be a polymeric material. See, for example, U.K. Patent Publication 2,066,839, Bares et al (applied for in the name of Vysoka Skola Chemicko Technologika), published July 15, 1981. These methods may also be used to mask unpleasant odors in a composition or to protect perfume from degradation by harsh components in a laundry composition. Such methods will provide these benefits only for dry powder or granular type compositions because, as soon as the polymer is hydrated the perfume is released. Thus, these methods provide for perfume fragrance benefits upon opening of the product package and loading into the washing apparatus. While these benefits are desirable, it would be even more desirable to have a method which allows for delivery of undiluted, undissipated and unaltered perfume to fabric and release of the perfume at the end of the laundry process so that the fabric is scented with the desirable perfume odor.

Of course, one method for achieving this end is putting the perfume into a product which goes directly into the dryer. This way, the perfume is delivered to the fabric in the dryer cycle. Such a method is taught in both U.S. Patent 4,511,495, Melville, issued April 16, 1985, and U.S. Patent 4,636,330, Melville, issued January 13, 1987. Both teach forming perfume into particles with a carrier. These particles are then formulated into a composition which is applied to textiles prior to putting into the dryer or prior to clothes-line drying.

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An even more desirable method for delivering perfume to laundered fabric would be one which provides for protection of the perfume through the washing process and hence delivery of the perfume to fabric in essentially its original state.

5 Such a method must allow for prevention of dilution, degradation or loss of the perfume during the wash cycle of the laundry process. This is done by utilizing a system that releases the perfume in the drying process or later after the perfume has been delivered to the fabric. Preventing release of perfume during the washing process involves very different and more difficult technology. Such protection must be stable in not only the heat-elevated conditions of the wash but must also be stable against degradation by water and other harsh chemicals in the washing process such as bleach, enzymes, surfactants, etc.

10 One method which has been developed to provide these benefits is perfume microencapsulation. Here the perfume comprises a capsule core which is coated completely with a material which may be polymeric. U.S. Patent 4,145,184, Brain et al, issued March 20, 1979, and U.S. Patent 4,234,627, Schilling, issued November 18, 1980, teach using a tough coating material which essentially prohibits the diffusion out of the perfume. The perfume is delivered to fabric via the microcapsules and is then released by rupture of the microcapsules such as would occur with manipulation of the fabric.

15 Another method of perfume delivery involves providing protection of perfume through the wash cycle, with release of perfume in the heat-elevated conditions of the dryer. U.S. Patent 4,096,072, Brock et al, issued June 20, 1978, teaches a method for delivering fabric conditioning agents to textiles through the wash and dry cycle via particles containing hydrogenated castor oil and a fatty quarternary ammonium salt. Perfume may be incorporated into these particles. However, it is not clear whether the perfume thus incorporated is released in the wash cycle or carried in the particles to the dryer and released there, as the particles soften.

20 25 30 35 U.S. Patent 4,402,856, Schnoring et al, issued September 6, 1983, teaches a microencapsulation technique which involves the formulation of a shell material which will allow for diffusion of

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5 perfume out of the capsule only at certain temperatures. This allows for maintenance of the perfume particles through storage and additionally through the wash cycle. The particles adhere to the fabric and are carried over to the dryer. Diffusion of the perfume out of the capsules then occurs only in heat-elevated conditions of the dryer. These particles are made of gelatin, an anionic polymer and a hardening agent.

10 U.S. Patent 4,152,272, Young, issued May 1, 1979, teaches incorporating perfume into waxy particles to protect the perfume through storage in dry compositions and through the laundry process. The perfume then diffuses through the wax matrix of the particles on the fabric in the heat-elevated conditions of the dryer.

15 It is desirable to provide compositions comprising perfume particles that can be incorporated in liquid as well as dry granular or powder compositions and provide long-term storage stability.

20 It is desirable to provide a method for delivering a broad range of perfume materials to fabric or other surfaces during a cleaning or fabric- or fiber-conditioning process.

25 It would be most desirable to have a perfumed cleaning or conditioning composition which would provide improved product odor, improved odor of perfume released during the cleaning process, and improved odor and intensity of perfume delivered to the surface being cleaned.

It would be particularly desirable to provide perfumed particles which are stable in fluid compositions, but which liberate their perfume, in use.

Summary of the Invention

30 Apart from being especially effective in providing their intended benefit of prolonged perfume release, the coated perfumed particles of the present invention are designed to provide several important advantages over the various encapsulated perfumes of the art. First, the preferred coatings used herein are stable not
35 only in solid or granular laundering compositions, but also in liquid compositions. Second, the coated perfumed particles herein do not require any additional treatment, such as the application of additional cationic coatings, to achieve the desired result of

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substantivity to fibers and fabrics. Third, using solid carrier materials as the "cores" of the particles herein makes the particles less fragile than perfume particles having liquid cores. This not only simplifies manufacture, but also means that the particles are more robust under storage and shipping conditions in laundering and other types of compositions. The nonpolymeric carrier materials used herein have the additional advantage over many polymeric perfume carriers in that they are degradable in the environment or in sewage treatment facilities and/or that they are available from renewable resources such as plant and animal fats and oils. Moreover, the particles herein allow for the formulation of condensed detergent granules with desirable perfume levels, but without the undesirably high odor levels in the product package that would be associated with the use of raw perfume.

However, in order to achieve the above-described benefits and yet function in the intended manner as a perfume delivery vehicle, it is important that the perfume-carrying materials employed herein be carefully selected from among the various classes of prospective perfume carrier materials broadly disclosed in the art. For example, the carrier should be somewhat polar so that it will imbibe a considerable amount of a wide variety of perfume ingredients. Fatty alcohols and esters meet this requirement, but fatty acids tend to be too polar to imbibe the desired high levels of many perfume ingredients. The carrier should be solid at room temperature so that stable particles can be produced and stored, yet must be somewhat softenable, in-use, to help release the perfume. Again, fatty alcohols and esters meet these requirements. Moreover, the carriers should be substantially water-insoluble (as defined more fully hereinafter) under usage conditions, since they would otherwise completely dissipate their perfume into the aqueous medium, e.g., laundry liquors, in which they are used. Fatty alcohols and esters also meet these requirements. It is also important that the core material be selected to be "compatible" with the material used to make the friable coating. This is especially important to provide coated particles with good integrity of the preferred friable aminoplast polymer coatings disclosed hereinafter. While not intending to be bound

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by theory, it appears that the polarity of the alcohols and esters makes them especially useful with such coatings.

Moreover, it has now been determined that the most highly preferred perfume particles of the present invention have optimal size requirements which are somewhat more stringent than various encapsulated perfumes known in the literature in order to perform optimally in laundering products of the type disclosed herein.

The present invention encompasses perfume particles having an average size, when coated, of less than about 350 microns (preferably, an average size not greater than 150 microns; most preferably a size range of 100-150 microns) which comprise from about 5% to about 50% (preferably, at least about 10%) of a perfume dispersed in from about 50% to about 95% of a nonpolymeric fatty alcohol or fatty ester, or mixtures thereof, carrier material having a molecular weight of from about 100 to about 500 and a melting point of from about 37°C to about 80°C, said esters or alcohols being substantially water-insoluble, said particles having a substantially water-insoluble friable coating on their outer surfaces. (By "size" herein is meant average particle diameter for substantially spherical particles, or the size of the largest diameter or dimension for nonspherical particles.) Particle sizes larger than this may be lost from the surface they are deposited on, and do not provide a relatively large enough surface area to release the perfume at the desired rate. Also, particles larger than specified herein may be undesirably noticeable on the surface being treated. Particles at the low end of the range tend to adhere well to the surface being treated, but tend to release the perfume quite rapidly. Extremely small particles outside the low end of the range tend to be rinsed off fabrics during laundering.

Typically, the particles herein are characterized by a coating which comprises up to about 30% by weight of the perfumed particles. For general use in fabric laundering and conditioning compositions, the coating typically comprises from 1% to 20%, preferably 10% to 20%, by weight of the perfumed particles.

Preferred particles herein are those wherein the friable coating is substantially water-insoluble. Suitable coatings of this type can be prepared from aminoplast polymers, e.g., the

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reaction products of an amine and an aldehyde. Typical friable coatings comprise, for example, the reaction products of an amine selected from urea and melamine, and an aldehyde selected from formaldehyde, acetaldehyde and glutaraldehyde, and mixtures of said amines and said aldehydes. Such friable coatings are described hereinafter.

The coated perfume particles herein are useful in situations where the particle coating is ruptured or worn away (e.g., in an automatic washing machine or laundry dryer) to release the particles, which, in turn, release their perfume. Thus, the coated particles are useful in typical cleaning composition, comprising detergent surfactants, optional builders, and the like. The particles are likewise useful in conditioning compositions, comprising fiber- and fabric-conditioning agents.

As can be seen from the foregoing and from the disclosures hereinafter, the present invention encompasses not only novel and useful perfumed particles and compositions containing same, but also encompasses a method for delivering perfume-releasing particles to the surface of fabrics undergoing a laundering or softening process in a laundering apparatus, comprising adding to said laundering apparatus a detergent composition or a fabric softening composition containing particles comprising the core/perfume/friable coating, as disclosed in detail herein, and operating said apparatus in standard fashion with agitation of the machine liquor and fabrics, whereupon the agitation associated with said operation ruptures the coating on said particles, or fractures the particles themselves, sufficiently to allow release of the perfume when said particles become deposited onto said fabrics during said laundering or softening process.

In a highly preferred mode, the process herein employs particles comprising: 55-65% by weight of the core material as a C_{14} - C_{18} alcohol, especially straight-chain alcohols, or mixtures thereof; from 20-30% by weight of the perfume; and the balance comprising a friable coating, especially water-insoluble polymeric coatings made from an amine such as urea, melamine, or mixtures thereof, plus an aldehyde selected from formaldehyde, glutaraldehyde, or mixtures thereof.

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It will be appreciated that the method herein is similarly useful in fabric bleaching operations which are carried out under conditions of sufficient agitation to fracture the friable coatings, or which rupture the particles themselves. Likewise, the method herein is suitable for releasing perfume particles from bar soap and/or shampoos, and the like, provided that such compositions are used, e.g., rubbed, with sufficient vigor to fracture the coating on said particles, or the particles themselves.

All percentages herein are by weight, unless otherwise specified.

Detailed Description of the Invention

The present invention allows for preservation, protection, and delivery of perfumes contained in cleaning and conditioning compositions through extended storage and harsh cleaning conditions. This is achieved by isolation of the perfume in a carrier material in the form of small particles. The individual components of the invention will now be discussed in detail.

The Perfumed Particles

The perfumed particles of the present invention comprise perfume dispersed in certain carrier materials. The perfumed particles are coated with a friable coating material which ruptures in-use to release the perfumed particle which, in turn, releases its perfume.

In the present context, the term "perfume" means any odoriferous material or any material which acts as a malodor counteractant. In general, such materials are characterized by a vapor pressure less than atmospheric pressure at ambient temperatures. The perfume or deodorant materials employed herein will most often be liquid at ambient temperatures, but also can be solids such as the various camphoraceous perfumes known in the art. A wide variety of chemicals are known for perfumery uses, including materials such as aldehydes, ketones, esters and the like. More commonly, naturally occurring plant and animal oils and exudates comprising complex mixtures of various chemical components are known for use as perfumes, and such materials can be used herein. The perfumes herein can be relatively simple in their composition or can comprise highly sophisticated, complex mixtures of natural and synthetic chemical components, all chosen to provide any desired odor.

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Typical perfumes herein can comprise, for example, woody/earthy bases containing exotic materials such as sandalwood oil, civet, patchouli oil and the like. The perfumes herein can be of a light, floral fragrance, e.g., rose extract, violet extract and the like. The perfumes herein can be formulated to provide desirable fruity odors, e.g., lime, lemon, orange and the like. Suitable perfumes include musk ambrette, musk ketone, musk tibetine, musk xylol, aurantiol, ethyl vanillin and mixtures thereof.

Perfume materials such as these are described more fully in S. Arctander, Perfume Flavors and Chemicals, Vols. I and II, Aurthor, Montclair, N.J., and the Merck Index, 8th Edition, Merck & Co., Inc. Rahway, N.J., both references being incorporated herein by reference.

In short, any chemically compatible material which exudes a pleasant or otherwise desirable odor can be used in the perfumed particles herein to provide a desirable odor when applied to fabrics.

Perfumes which are normally solid can also be employed in the present invention. These may be admixed with a liquefying agent such as a solvent prior to incorporation into the particles, or may be simply melted and incorporated, as long as the perfume does not sublime or decompose upon heating.

The invention also encompasses the use of materials which act as malodor counteractants. These materials, although termed "perfumes" hereinafter, may not themselves have a discernible odor but can conceal or reduce any unpleasant odors. Examples of suitable malodor counteractants are disclosed in U.S. Patent No. 3,102,101, issued August 27, 1963, to Hawley et al.

The perfumed particles of the present invention can even comprise perfumes which are not typically used to deliver a fragrance to a surface, such as fabric through the laundry process. Perfume materials which are very volatile, unstable, or soluble in the particular compositions being used to deliver the perfume may be used in the present invention because the perfume is isolated from the composition in the particles. Perfume materials which are not substantive to fabrics in the laundry process can also be used in the present invention since the

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particles deliver the perfume to the fabric surface where it is released. Thus, use of the present invention to deliver a perfume to a surface broadens the class of perfume materials that can be utilized.

5 Generally, the perfumed particles of the present invention will comprise from about 5% to about 50%, preferably from about 20% to about 30%, perfume. The exact amount of perfume used in the particles will vary greatly depending on the strength of the particular fragrance used, and the desired odor effect.

10 The carrier materials employed herein are characterized by several criteria which make them especially suitable in the practice of this invention. Of course, toxicologically-acceptable and non-skin irritating materials are used. As noted above, degradable materials and/or materials which are available from
15 renewable resources are used. In general, the materials are solids at room temperature have a melting point within the range noted hereinabove. This will prevent melting of the particles in storage. (It is most desirable to have a carrier material that will not completely melt in an automatic dryer, to avoid blocking
20 of the lint screen and excessive build-up of heat in the dryer). The melting point of the carrier material should also not be higher than a point at which the perfume to be combined therewith will decompose. The melting point of the carrier material is measured by what is called the drop melting point method.
25 American Society for Testing and Materials (ASTM) Test Method D127-63 (reapproved 1982, incorporated by reference herein). Briefly, this method involves the following. The sample to be measured is deposited onto a thermometer bulb by dipping a chilled thermometer into the melted sample. The thermometer bearing the
30 sample is then placed into a test tube and heated by means of a water bath until the sample melts and the first drop falls from the thermometer bulb. The average of the temperatures at which the drops of sample fall is the drop melting point of the sample.

35 The carrier material should also be inert to the perfume and relatively odorless. The material must allow for diffusion of the perfume therethrough. The carrier material must also be such that it melts without decomposition.

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Having thus described the carrier materials useful herein with regard to their physico-chemical properties, the following illustrates various nonpolymeric compounds which can be used as carrier materials herein.

5 One class of carrier materials which is highly preferred herein comprises the fatty alcohols. The fatty alcohols of chain length of at least C_{14} are substantially water-insoluble. Substantial water-insolubility is an important feature of the carrier materials in-use, since if the particle dissolves, e.g., in a
10 laundering liquid, it releases its perfume immediately and thus does not deposit onto fabrics to provide the intended prolonged release of said perfume. Accordingly, by "substantially water-insoluble" herein is meant that the carrier materials will not be dissolved in water to an extent greater than about 10%, preferably
15 not greater than 5%, by weight, at the temperatures of the aqueous media in which they are used.

Moreover, fatty alcohols are typically solid at room temperature, i.e., they have a melting point above about 30°C , and typically will melt over the range of about 37°C to about 75°C .
20 The most highly preferred carrier materials of this class will be selected from molecules which will not undesirably interact with the perfumes which they are carrying, nor have a substantial amount of undesirable odor characteristics of their own. For example, the preferred alcohol carriers described hereinafter
25 will, in general, preferably not be contaminated with lower molecular weight alcohols or fatty acids which could result in "goaty" or rancid odors, unless, of course, such odors are a desired complement to the perfume being carried. In particular, the straight-chain fatty alcohols are preferred, since they are
30 available from natural sources. However, branched-chain and some unsaturated alcohols may also be used.

Among the fatty alcohol class of carriers, those in the C_{14} - C_{18} chain length are most preferred. For reasons of possible malodor, as noted above, it is generally preferred that the
35 alcohols be substantially free of C_4 - C_{10} chain-length alcohols and their fatty acid oxidation products. More specifically, $n\text{-}C_{14}\text{OH}$ (myristyl alcohol/tetradecanol) is preferred under lower temperature laundering conditions in the United States, whereas C_{16} - C_{18}

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alcohols can be used under the somewhat higher temperature laundering conditions found in some European countries. Higher alcohols are also desirable where a long-lasting perfume benefit is desired. C₁₂ alcohols can also be present in the cores. However, it will be appreciated that cores containing substantial amounts of C₁₂ alcohols may liquify under some warehouse storage conditions, and the resulting liquid core/coated particles are more fragile than solid core/coated particles, and are subject to fracture when the product is shipped. The C₂₀-C₂₄ alcohols are also useful under some conditions, although these latter materials are in considerably shorter supply than the C₁₄-C₁₈ materials and are, consequently, more expensive. Mixtures of the fatty alcohols may also be used, provided that they meet the above-noted criteria.

In addition to the alcohols noted hereinabove, the following are representative, nonlimiting examples of alcohols which can be used as the core materials herein: n-pentadecanol, n-hexadecanol, n-heptadecanol, n-octadecanol, n-docosanol, n-heneicosanol, 16-methylheptadecanol, 26-methylheneicosanol, 22-methylpentacosanol, and D-18-methyleicosanol.

Other nonlimiting examples of nonpolymeric carrier materials useful herein include various esters having melting points of at least about 30°C, preferably from about 37°C to about 75°C. The same considerations regarding substantial water-insolubility, acceptable odor characteristics, etc., noted for the alcohols are also important factors to be considered with the ester perfume carrier materials.

In general, the esters will comprise at least about 18 carbon atoms. Suitable esters include, for example, lower (typically C₁-C₄) alkyl esters of fatty acids which, chemically, comprise fatty acid esters of lower monohydric alcohols. Likewise, various fatty acid esters of polyhydric alcohols can be employed herein, as long as the water-insolubility parameter is met. Fatty acid triglycerides, e.g., "fats", meeting the foregoing parameters are also suitable for use herein, assuming proper deodorization.

The following examples of suitable ester carrier materials are given by way of illustration, and not by way of limitation. It will be appreciated by those skilled in the art that such

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esters are commercially available from various sources. Such esters include: methyl stearate; ethyl stearate; methyl nonadecylate; ethyl nonadecylate; methyl arachidate; methyl behenate; the monostearyl and monopalmityl esters of ethylene glycol; the monostearyl and monopalmityl esters of propylene glycol; the monostearyl and monopalmityl esters of trimethylene glycol. Various diesters of the foregoing polyols can also be used, based on their melting points and solubility characteristics.

In a typical process, the perfume-containing particles can be made as follows. The carrier material is first heated slowly to its melting point. The material is not heated any more than is necessary to just melt the substance. The perfume is then quickly added, generally as an oil or liquid, at room temperature to the melted carrier substance. The two are quickly mixed into a homogeneous blend then rapidly cooled with liquid nitrogen (or with dry ice or any other means which will cool the mixture quickly) until it has completely solidified. The solid material is then subdivided, generally by grinding or milling, to produce particles of the desired average size. Other methods such as spray cooling or extrusion may also be used to subdivide the particles.

To further stabilize particularly volatile or delicate perfumes, it may be desirable to preload the perfume (i.e., mix the perfume) onto silica gel or clay prior to combining with the carrier substance. Some perfumes which are not so volatile will not require this special treatment because it would inhibit their release from the carrier substance too much. Optimization of the rate at which the perfume is released from the carrier is the goal, and this optional additional step allows for better control of that rate with some of the more volatile perfumes.

The Coating

The perfume-containing particles, above, are encapsulated to provide a friable coating. This coating prevents the perfume from diffusing out of the particles as readily during long storage periods. Moreover, the coating helps preserve the original "character" of perfumes having particularly volatile top-notes. Moreover, the coating helps protect the perfumed particle from other ingredients in the formulation being perfumed.

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The coating materials used herein are friable, and are designed to break-up as the perfumed formulation is used, thereby releasing the perfumed particle.

5 The particles may be coated with more than one friable coating material to produce a particle having more than one layer of coating. Different coating materials can be chosen to provide different perfume protection as needed, so long as one of the coatings, generally, the outermost, is friable.

10 The individual perfume-containing particles may also be agglomerated with the coating material to provide larger particles which comprise a number of the individual perfume-containing particles. This agglomerating material surrounding the particles provides an additional barrier to diffusion of the perfume out of the particles. Such an approach also minimizes the surface area of free particles susceptible to perfume diffusion. The ratio of
15 perfume particles to agglomerate material will vary greatly depending upon the extent of additional protection desired. This agglomeration approach may be particularly useful with very volatile perfumes or perfumes that are especially susceptible to degradation. Also, agglomeration of very small perfume particles
20 would provide additional protection against premature diffusion out of perfume.

25 Agglomeration of particles in this fashion is useful in preventing segregation of small perfume particles from larger detergent granules, for example, in a dry granular detergent product.

30 Process of Manufacture - For friable coatings, the process of manufacture is based on applying the coating as a kind of "shell" to the perfumed particles. For perfumed particles whose carrier material has a melting point below that of the boiling point of the solvent used in the process, the process involves adding the carrier and perfume to a solvent solution of the "shell" material, or a suitable precursor, held above the carrier melting
35 temperature. The system is agitated sufficiently to form an emulsion of the carrier/perfume of desired liquid drop size in the shell solution. The conditions necessary to deposit the encapsulating material are then established and the whole is cooled to give encapsulated solid particles having the desired,

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friable "shell". Water insolubility of the shell is established either at the deposition stage, or by suitable treatment prior to isolation or use of the particles.

Although the process described here is a one step molten drop formation/encapsulation procedure, it should be readily apparent to those skilled in the art that encapsulation of pre-formed perfume particles can be accomplished in a like manner. The pre-formed particles can be prepared in a variety of ways, including cryogrinding, spray drying, spray congealing and meltable dispersion techniques such as those described in books by P. B. Deasy ("Microencapsulation & Related Drug Processes", Dekker, N.Y., 1986) and A. Kondo ("Microcapsule Processing and Technology", Dekker, N.Y., 1979). Such techniques would be required for carrier materials having a melting point above the solvent boiling point.

A variety of suitable encapsulation procedures can be used, such as reviewed in the books by Deasy and Kondo above. Depending on materials used, the shell can impart hydrophilicity or hydrophobicity to the particles. For examples of encapsulating materials and processes including gelatin-gum arabic concentrate deposited by a complex coacervation procedure, see, e.g., U.S. Patent 2,800,457, and urea-formaldehyde deposited by a polycondensation process, e.g., U.S. Patent 3,516,941. Water insolubility of shell materials may be imparted, for example, by cross-linking of gelatin-gum arabic coacervate with suitable aldehydes or other known gelatin hardeners after deposition. Polymerization of the urea-formaldehyde precondensate during an encapsulation process inherently yields water-insolubility.

The slurry containing the perfume particles can be used directly, e.g., admixed and dried with other components of the granular detergent formulations, or the particles can be washed and separated, and dried if desired.

Example I

Perfume particles containing a hydrophobic, water-insoluble, friable coating deposited by polycondensation are prepared as follows.

A urea-formaldehyde precondensate is first formed by heating a mixture of 162 g 37% aqueous formaldehyde and 60-65 g urea,

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adjusted to pH 8.0 with 0.53 g sodium tetraborate, for 1 hour at 70°C, and then adding 276.85 g water.

429 ml of this precondensate and 142 ml water are then stirred in a 1-l steel reactor and 57.14 g sodium chloride and 0.57 g sodium carboxymethyl cellulose added. Then are added the core components comprising 166.2 g C₁₄OH carrier and 55.8 g perfume, and the reactor is heated to about 90°C. Agitation is adjusted to emulsify and maintain the molten core at the desired drop size, and the pH of the contents is adjusted to about 5.0 with dilute hydrochloric acid.

The reactor is then allowed to cool to room temperature with a gradual pH reduction to 2.2 over a 2 hour period. The reactor is then increased to about 50°C for a further 2 hours, then cooled to room temperature, after which the pH is adjusted to 7.0 with 15% N ammonium hydroxide solution.

The resultant slurry containing the solid core particles encapsulated with urea-formaldehyde polymer may be used directly, or may be isolated by separation, washing and air drying as required.

The coated perfumed particles prepared in the foregoing manner can be used in all types of products where it is desirable to deposit fragrances on treated surfaces, and wherein sufficient agitation or pressure is exerted to rupture the friable coating. Typical examples of such products are laundry detergents and fabric softeners. The following illustrates the use of the compositions of this invention in such products.

Laundry cleaning products comprise: a deterative surfactant (typically 5%-30% wt.); optionally but typically, one or more detergency builders (10%-55% wt.); optionally, 3%-20% wt. of various enzymes, bleaches, carriers, and the like, all well-known from standard texts and very familiar to detergent formulators. Surfactants include soap, alkyl benzene sulfonates, ethoxylated alcohols, alkyl sulfates, alpha-sulfonated fatty acids, and the like. Builders include various phosphates, zeolites, polycarboxylates and the like. U.S. Patents 3,985,669, 4,379,080 and 4,605,609 can be referred to for typical listings of such ingredients.

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Modern fabric softeners typically comprise about 3%-35% wt. of one or more quaternary ammonium salts, e.g., ditallowdimethyl ammonium chloride or imidazoline or imidazolinium compounds. Softeners (and antistatic agent) generally have one, or preferably two, C₁₂-C₁₈ alkyl substituents and two or three short chain alkyl groups. Again, such materials are conventional and well-known to softener formulators.

It is to be understood that one of the major advantages of the coated perfumed particles of this invention is their ability to be stably formulated (typically 0.1%-10% wt.) in combination with conventional detergent, bleach and fabric treatment compositions without difficulty.

Example II

A granular laundry detergent is as follows:

<u>Component</u>	<u>Weight %</u>
Sodium C ₁₃ alkylbenzene sulfonate	7.5
Sodium C ₁₄₋₁₅ alkylsulfate	7.5
C ₁₂₋₁₃ alkyl polyethoxylate (6.5) stripped of unethoxylated alcohol and lower ethoxylate	2.0
C ₁₂ alkyltrimethyl ammonium chloride	1.0
Sodium tripolyphosphate	32.0
Sodium carbonate	10.0
Sodium perborate monohydrate	5.3
Sodium octanoyloxybenzene sulfonate	5.8
Sodium diethylene triamine pentaacetate	0.5
Sodium sulfate, H ₂ O and minors	Balance

The above composition is prepared using conventional means. The composition is combined with the perfume particles of Example I as follows. An amount of the perfume particles of Example I is combined with the detergent composition so that the detergent composition comprises about 0.3% perfume.

The particles may be simply mixed in with the detergent granules. To prevent segregation of the perfume particles during packaging and shipping (due to their smaller size relative to the detergent granules), the particles can optionally be coated or agglomerated with a water-soluble coating material (on top of the friable coating) prior to combining with the detergent granules. This can be accomplished with a Schugi mixer (Flexomix 160) where

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a sufficient amount of a dextrin glue solution (2% dextrin, 3% water) is sprayed onto the particles to result in agglomerates of perfume particles in the same size range as other detergent granules.

5 The perfume is protected in the particles from degradation by the bleach in the detergent composition over long periods of storage. When used in the laundry process in an automatic washing machine this detergent composition will provide perfume fragrance in substantially its original state from product, through the wash
10 process and onto the fabric.

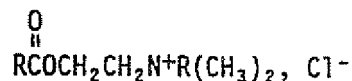
A great number of perfumes can be utilized in the present composition that would not otherwise be appropriate for use in such laundry detergent compositions.

Example III

15 A liquid fabric softener for use in an aqueous laundry rinse bath is as follows:

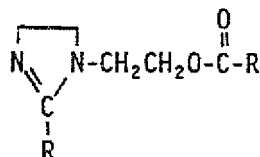
<u>Component</u>	<u>Weight %</u>
Softener A*	3.00
Softener B**	5.00
20 HCl	0.29
Polydimethylsiloxane	0.15
Polyethylene Glycol (4000)	0.30
Bronopol (Antimicrobial)	100 ppm
Calcium Chloride	30 ppm
25 Dye	30 ppm
Coated Perfume Particles***	4.0
Water	Balance

*Softener A is



30 wherein each R group is in the C₁₅-C₁₈ alkyl range.

**Softener B is



35 wherein each R group is in the C₁₅-C₁₈ alkyl range.

***Particles prepared according to Example I. 80-100 micron size range; 20% coating weight.

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When used in the rinse bath of an automatic washing machine, the coating on perfumed particles of Example III is ruptured and the particles provide a fragrance to the fabrics being treated.

Example IV

5	A liquid laundry detergent composition is as follows.	
	<u>Component</u>	<u>Weight %</u>
	C ₁₃ linear alkylbenzene sulfonic acid	7.2
	C ₁₄₋₁₅ alkyl polyethoxylate (2.25)	
	sulfuric acid	10.8
10	C ₁₂₋₁₃ alcohol polyethoxylate (6.5)*	6.5
	C ₁₂ alkyl trimethylammonium chloride	1.2
	C ₁₂₋₁₄ fatty acid	13.0
	Oleic acid	2.0
	Citric acid (anhydrous)	4.0
15	Diethylenetriamine pentaacetic acid	0.23
	Protease enzyme (2.0 AU/g)	0.75
	Amylase enzyme (375 Am. U/g)	0.16
	TEPA-E ₁₅₋₁₈ **	1.5
	Monoethanolamine	2.0
	(moles of alkanolamine)	(0.033)
20	Sodium ion	1.66
	Potassium ion	2.65
	(molar K+:Na+)	(0.94)
	Propylene glycol	6.8
25	Ethanol	7.8
	Formic acid	0.66
	Calcium ion	0.03
	Minors and water	Balance to 100
	pH at concentration of 10%	
30	in water at 68°F (20°C)	8.65

*Alcohol and monoethoxylated alcohol removed.

**Tetraethylene pentamine ethoxylated with 15-18 moles (avg.) of ethylene oxide at each hydrogen site.

The detergent is prepared by adding the components, with continuous mixing, in the following order: paste premix of alkylbenzene sulfonic acid, sodium hydroxide, propylene glycol and ethanol; paste premix of alkyl polyethoxylate sulfuric acid,

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5 sodium hydroxide and ethanol; pentaacetic acid; alcohol polyethoxylate; premix of water, brighteners, alkanolamine and alcohol polyethoxylate; ethanol; sodium and potassium hydroxide; fatty acid; citric acid; formic acid and calcium; alkyl trimethylammonium chloride; TEPA-E₁₅₋₁₈; adjust pH to about 8.1; and balance of components.

10 The above composition is combined with the perfume-containing particles prepared according to Example I as follows. An amount of the perfume particles of Example I (avg. size range 40-150 microns; 5% coating) is thoroughly mixed into the liquid detergent composition so that the detergent composition comprises about 0.3% perfume (about 1% of the detergent composition will comprise the perfume particles).

Example V

15 A fiber- and fabric-softener composition is as follows.

	<u>Component</u>	<u>Weight %</u>
	Softener C*	3.7
	TAMET**	0.3
	GMS***	1.20
20	Phosphoric Acid	0.023
	Polydimethylsiloxane (350)	0.10
	Glutaraldehyde	550 ppm
	Blue Dye	10 ppm
	Coated Perfume Particles****	3.0

25 *(R¹)₂(CH₃)₂N⁺, Br⁻, wherein R¹ is mixed C₁₂-C₁₈ alkyl (i.e., "tallowalkyl").

**TAMET is tallowalkyl N(CH₂CH₂OH)₂.

***GMS is glyceryl monostearate.

30 ****Coated perfume particles per Example I, sieved to average size less than 100 microns. Coating weight 20%.

It will be appreciated by those skilled in the art that the anions, X, used with any of the cationic fabric softeners herein are a routine matter of choice, and that X can be, for example, chloride, bromide, methylsulfate, and the like. Mixtures of fabric softeners can be used, as can mixtures of anions.

Example VI

The fabric softener composition of Example III is modified by using perfumed particles with friable coatings (melamine/urea/formaldehyde; 0.1/1/1.1 mole ratio; 80 micron size) with coating

- 21 -

weights of about 20%, respectively. It is to be noted that melamine substitution for about 15% of the urea in the aminoplast coatings is preferred for use in fabric softeners. It is also to be noted that particles above about 80 microns are visible in softener products.

5

Example VII

A deterative bar composition is prepared by gently (so as not to fracture the coating) admixing 2% by weight of the coated perfumed particles of Example I (7% coating; all particles through 150 micron sieve) into a 99.44% tallow soap mixture (Na salt) and formed into a bar in a pin die.

10

The compositions herein can also be used in combination with abrasives. As is well-known, abrasive cleaners typically comprise 10% to 90% abrasive such as pumice, silica, calcium carbonate, and the like. Coated perfume particles used in such cleaners are ruptured, in-use, to release their perfume.

15

Example VIII

An abrasive cleanser is as follows.

	<u>Component</u>	<u>Weight %</u>
20	Sodium tallow sulfate	1.0
	Calcium carbonate	40.0
	Pumice (through 60 micron sieve)	45.0
	Sodium sulfate	10.0
	Coated perfume particles*	3.0
25	Chlorinated trisodium phosphate	1.0

*Per Example I; 10% coating; particles through 100 micron sieve.

The composition of Example VIII is prepared by gently dry-blending the ingredients.

It will be appreciated by the formulator that the weight (or thickness) of operable friable coatings can be adjusted according to the usage envisioned. For example, even relatively thick coatings will rupture and release their perfume particles under European machine washing conditions, which can involve wash times of many minutes, at high temperature and considerable agitation. By contrast, USA machine washing conditions are much shorter, and milder, so less coating material should be used. For fabric softeners, agitation and agitation times are usually less than for washing.

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Example IX

A bleach composition comprises ca. 6% aqueous hypochlorite/
H₂O containing 10% (wt.) of the particles of Example I. The
product is shaken prior to use as a clothes bleach or toilet bowl
disinfectant to suspend the particles.

Example X

A granular laundry detergent is as follows.

	<u>Component</u>	<u>Weight %</u>
	C ₁₂ alkylbenzene sulfonate	5.64
10	Tallow alcohol sulfate	2.42
	Sodium sulfate	22.00
	Sodium silicate	8.00
	Magnesium sulfate	0.40
	Carboxymethyl cellulose	0.29
15	EDTA	0.29
	Brightener 47	0.15
	Sodium tripolyphosphate	21.34
	C ₁₄₋₁₅ E07 surfactant*	5.00
	Sodium perborate 4H ₂ O	13.23
20	Sodium perborate 1H ₂	1.96
	Sodium carbonate	7.00
	Proteolytic enzyme	0.79
	TAED**	3.03
	Perfume particles***	1.00
25	Water/minors	Balance

*As Dobanol 45-7

**Tetraacetylenediamine

***Prepared per Example I; 100-150 micron size; 20% coating

Example XI

A concentrated detergent granule is as follows.

	<u>Component</u>	<u>Weight %</u>
30	Sodium linear alkyl benzene sulfonate with an average chain length of 12.4	13.9
35	Sodium alkylsulfate with an average chain length of 14.5	5.9
	Aluminosilicate (Zeolite A; 1-10 micron)	25.36
	Polyacrylate 4500	4.47
	Polyethylene glycol 8000	1.46

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	Sodium carbonate	17.82
	Sodium sulfate	11.06
	Silicate solids	2.05
	Brightener 15	0.29
5	Moisture	7.70
	Miscellaneous	0.57
	Enzyme	0.78
	Nonionic - C ₁₂₋₁₃ EO _{6.5}	1.07
	Citric acid	6.57
10	Perfume particles*	1.00

*Per Example I; 100-150 micron size

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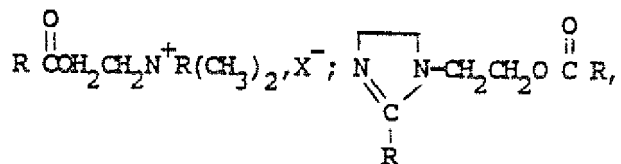
35

CLAIMS:

1. Coated perfume particles having an average size, when coated, of less than 350 microns, preferably not greater than 150 microns, characterized in that said particles comprise from 5% to 50% by weight of a perfume dispersed in from 50% to 95% by weight of a nonpolymeric solid fatty alcohol or fatty ester carrier material, or mixtures thereof, said alcohol or ester having a molecular weight of from 100 to 500 and a melting point of from 37°C to 80°C, said alcohol or ester being substantially water-insoluble, said particles having a substantially water-insoluble friable coating on their outer surfaces.
2. The particles of Claim 1 wherein the coating comprises an aminoplast polymer.
3. The particles of Claim 2 wherein the coating comprises the reaction product of an amine and an aldehyde, preferably an amine selected from urea and melamine, and an aldehyde selected from formaldehyde, acetaldehyde and glutaraldehyde, and mixtures of said amines and said aldehydes.
4. The particles of Claim 3 wherein the carrier material comprises an alcohol selected from the C₁₄-C₁₈ alcohols.
5. A detergent composition, comprising one or more deterative surfactants, and optionally, one or more builders, said composition being characterized in that it contains coated perfume particles according to Claim 1.
6. A detergent composition according to Claim 5 wherein said perfume particles comprise a C₁₄-C₁₈ fatty alcohol coated with a friable aminoplast polymer which comprises the reaction product of an amine selected from urea, melamine, or mixtures thereof and an aldehyde selected from formaldehyde, acetaldehyde, glutaraldehyde, or mixtures thereof.

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7. A detergent composition according to Claim 5 which is in granular form, in bar form, or which additionally contains an abrasive.
8. A fabric softener composition, comprising one or more fabric- or fiber-softening or antistatic agents, characterized in that said composition contains coated perfume particles according to Claim 1.
9. A softener composition according to Claim 8 wherein said perfume particles comprise a C_{14} - C_{18} alcohol and wherein said friable coating is the reaction product of an amine selected from urea and melamine, or mixtures thereof, and an aldehyde selected from formaldehyde, acetaldehyde, glutaraldehyde, or mixtures thereof.
10. A softener composition according to Claim 9 comprising said perfume particles and a fabric- or fiber-softening or antistatic agent selected from



wherein each R is in the C_{15} - C_{18} alkyl range; and $(\text{R}^1)_2(\text{CH}_3)_2\text{N}^+\text{X}^-$, wherein each R^1 group is C_{12} - C_{18} alkyl; and mixtures thereof; and wherein X is an anion.

11. A method for delivering perfume-releasing particles to the surface of fabrics undergoing a laundering or softening process in a laundering apparatus, characterized in that said method comprises adding to said laundering apparatus a detergent composition or a fabric softening composition containing particles according to Claim 1, and operating said apparatus in standard fashion with agitation of the machine liquor and fabrics, whereupon the agitation associated with said operation ruptures the coating on said particles, or fractures the particles themselves, sufficiently to allow release of the perfume when said particles become deposited onto said fabrics during said laundering or softening process.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US91/00905

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all):		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC(5): C11D 3/50		
US CL.: 252/90,174,174.11,174.13,174.23		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
US	252/90,174,174.11,174.13,174.23	
Documentation Searched other than Minimum Documentation to the extent that such documents are included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹		
Category *	Citation of Document, ¹ with indication, where appropriate, of the relevant passages ²	Relevant to Claim No. ³
A	US, A, 4,234,627 (SCHILLING) 18 November 1980 See column 14, claim 1 and claim 2; column 3, line 15 and column 14, line 56; column 5, line 51-57.	1-11
A	US, A, 4,145,184 (BRATN et al.) 20 March 1979 See column 12, claims 1,3,5 and column 2, line 34.	1-11
A	US, A, 4,636,330 (MELVILLE) 13 January 1987 See column 1, lines 50-60, column 2, line 50; column 4, lines 20-25; column 6, lines 45-50.	1-11
A	US, A, 4,152,272 (YOUNG) 01 May 1979 See column 12, claim 1; column 3, line 50; column 2, line 45.	1-11
<p>* Special categories of cited documents: ¹</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
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(54) Title: MALODOR-CONTROLLING COMPOSITIONS COMPRISING ODOR CONTROL AGENTS AND MICROCAP-
SULES CONTAINING AN ACTIVE MATERIAL

(57) Abstract: Malodor-controlling compositions comprise microcapsules containing an active material and/or an optional odor
control agent, an odor control agent outside of the microcapsules, and an aqueous carrier. The active material is preferably a perfume
and the composition provides a controlled-release scent, along with controlling malodor. Methods of reducing or removing malodor
from a surface having malodor comprise the step of contacting the surface with a malodor-controlling composition comprising mi-
crocapsules containing an active material and an odor control agent.

MALODOR-CONTROLLING COMPOSITIONS COMPRISING ODOR CONTROL AGENTS AND MICROCAPSULES CONTAINING AN ACTIVE MATERIAL

TECHNICAL FIELD

The present invention relates to malodor-controlling compositions that can be applied to surfaces, including household surfaces such as carpets, fabrics, and the like, for reducing or removing malodor on the surface and for providing a controlled-release of an active material, preferably a perfume scent, into the environment surrounding the surface.

BACKGROUND OF THE INVENTION

Fabric refresher products have become a popular product in today's consumer goods market. Such products typically involve a liquid composition that is sprayed onto surfaces, such as fabrics, to reduce or remove malodor from the surfaces. Some of these products can also provide a pleasing scent by incorporation of perfume into the composition. However, such products typically are not capable of providing a controlled-release of an active material, such as a perfume scent.

Other products merely provide a pleasant fragrance, but do not act to reduce or remove malodor. Instead, such products utilize strong perfume scents to mask malodors by providing a scent stronger than the malodor. JP 03-173,565 ("JP '565") discloses an encased-perfume spray composition wherein the perfume is encased in microcapsules. The spray composition is preferably an aerosol-type composition utilizing a propellant. The perfume-encased microcapsules adhere to clothes, carpets, neckties, etc., and the fragrance is slowly released or is released by pressure such as friction. The spray compositions of JP '565 provide a pleasant fragrance, but do not address the problem of reducing or removing malodor from surfaces.

JP 11-246383 ("JP '383") similarly discloses a composition made of a slurry of microcapsules containing essential oils mixed with an aqueous binder. The compositions can be applied to fibers, such as bedding sheets, in which the fragrance can be released from the microcapsule, e.g., during movement as a person sleeps. However, as with the spray compositions of JP '565, the compositions of JP '383 provide a pleasant fragrance, but do not address the problem of reducing or removing malodor from surfaces.

US 4,520,142 ("US '142") discloses microencapsulated liquids, such as perfumes, that are applied to substrates from an aerosol applicator. The aerosol compositions of US '142 contain a microcapsule containing liquid, a polymeric binder, a solvent for the polymeric binder, and an aerosol propellant. However, while the aerosol compositions of US '142 provide a controlled-

release of a liquid material, the compositions do not address the problem of reducing or removing malodor from surfaces.

There has thus been a need to provide a composition that is able to reduce or remove malodors from surfaces, while providing a controlled-release of an active material, preferably a perfume scent, into the environment surrounding the surface. The present invention addresses this previously unmet need.

SUMMARY OF THE INVENTION

The present invention relates to malodor-controlling compositions comprising microcapsules containing an active material and/or an optional odor control agent, an odor control agent outside of the microcapsules, and aqueous carrier. The malodor-controlling compositions can be applied to surfaces, such as fabrics, to reduce or remove malodor from the surface and to provide a controlled-release of the active material onto the surface or into the environment surrounding the surface. The active material is preferably a perfume and the composition controls malodor and provides a controlled-release scent.

The invention further relates to methods of using malodor-controlling compositions comprising the step of contacting a surface with the malodor-controlling compositions.

The invention further relates to a process for making a malodor-controlling composition comprising an odor control agent and microcapsules containing an active material.

The present invention further relates to the use of a malodor-controlling composition comprising an odor control agent and microcapsules containing an active material to reduce or remove malodor from a surface and/or to provide a controlled-release of the active material.

All documents cited herein are, in relevant part, incorporated herein by reference; the citation of any document is not to be construed as an admission that it is prior art with respect to the present invention.

It should be understood that every maximum numerical limitation given throughout this specification will include every lower numerical limitation, as if such lower numerical limitations were expressly written herein. Every minimum numerical limitation given throughout this specification will include every higher numerical limitation, as if such higher numerical limitations were expressly written herein. Every numerical range given throughout this specification will include every narrower numerical range that falls within such broader numerical range, as if such narrower numerical ranges were all expressly written herein.

All parts, ratios, and percentages herein, in the Specification, Examples, and Claims, are by weight and all numerical limits are used with the normal degree of accuracy afforded by the art, unless otherwise specified.

DETAILED DESCRIPTION OF THE INVENTION

The malodor-controlling compositions of the present invention comprise microcapsules containing an active material (preferably perfume) and/or an optional odor control agent (which may be referred to herein as an "encapsulated odor control agent"), an odor control agent outside of the microcapsules, and aqueous carrier.

It should be understood that the encapsulated odor control agent need not be completely encapsulated (that is, in some embodiments, it may be partially encapsulated). The same is true for the microcapsules containing the active material.

There are a non-limiting number of embodiments of the compositions described herein. These embodiments include, but are not limited to embodiments in which at least some of the same microcapsules contain both an active material and the optional odor control agent therein. In other embodiments, the composition may comprise a group of microcapsules that contain an active material, and different microcapsules that contain the optional odor control agent. The composition may comprise microcapsules with different types of shells or coating materials. In addition, in some embodiments, the encapsulated odor control agent and the odor control agent outside of the microcapsules may be the same odor control agent. In other embodiments, they may be different odor control agents.

The present compositions can also contain a wide variety of additional optional ingredients such as dispersants, solvents, aerosol propellants, surfactants, free perfume, antimicrobial actives/preservatives, wrinkle control agents, and the like. The compositions can be used to reduce or remove malodor from surfaces (especially fabrics) and provide a controlled-release of the active material. When the active material is a perfume, the present compositions provide a controlled-release scent.

MICROCAPSULES CONTAINING AN ACTIVE MATERIAL

The present compositions comprise microcapsules containing an active material and/or an optional odor control agent. The microcapsules provide a controlled-release of the active material and/or an optional odor control agent contained in the microcapsule. The microcapsules in the compositions of the present invention can be any ruptureable capsule containing an active material therein and/or an optional odor control agent or capsule which is controllably penetrable by the active material or odor control agent encapsulated therein. The rupture strength of the microcapsules should be within a range that can endure handling and spraying without rupturing and yet break by applying a force of friction across the surface being treated with the composition.

The shell of the microcapsules can be made from a wide variety of materials. Such materials are typically polymeric and are designed to resist becoming solubilized in the chemical

matrix of the present compositions. Non-limiting examples of materials suitable for making the shell of the microcapsules herein include urea-formaldehydes, melamineformaldehydes, phenolformaldehydes, gelatin, poly(vinyl alcohol), poly(vinyl pyrrolidone), polyacrylates, polyamides, polyurethane, polymethacrylates, polyepoxides, cellulose acetate, cellulose nitrate, cellulose acetate butyrate, ethyl cellulose polyester, polychlorotrifluoroethylene (e.g. KEL-F), ethyl/vinyl acetate, saran, polystyrene, zein, paraffin wax, animal wax, vegetable wax, microcrystalline wax, polyethylene wax, and the like. Preferred microcapsule shell materials include poly(oxymethyleneurea), poly(oxymethylenemelamine), gelatin, polyurethane, *poly(vinyl alcohol)*, and mixtures thereof. Other suitable microcapsule shell materials are disclosed in, e.g., U.S. Patent Nos. 2,800,458; 3,159,585; 3,516,846; 3,533,958; 3,697,437; 3,888,689; 3,996,156; 3,965,033; 4,010,038; 4,016,098; 4,087,376; 5,591,146; UK Patent Nos. 2,006,709 and 2,062,570; and Benita, Simon (ed.), MICROENCAPSULATION: METHODS AND INDUSTRIAL APPLICATIONS (Marcel Dekker, Inc. 1996).

The size of the microcapsules can be important in the usefulness of microcapsules according to the practice of the present invention. Generally, the microcapsules will have an average diameter of from about 0.001 to about 1,000 microns, preferably from about 1 to about 500 microns, more preferably from about 10 to about 100 microns, and even more preferably from about 20 to about 70 microns. These dimensions can play an important role in the ability to control the application of capsules in the practice of the present invention. The broadest range of capsule size under any conditions would be about 0.001 to about 1,000 microns and a more easily sprayed size limit would be between about 20 and about 70 microns.

In general, the present compositions can comprise microcapsules at a wide variety of levels. Microcapsules are typically included in the present compositions at a level of from about 0.001% to about 99.9%, preferably from about 0.005% to about 50%, and more preferably from about 0.01% to about 20%, by weight of the composition. When the compositions are aqueous liquid compositions (especially non-aerosol compositions) to be sprayed onto surfaces, such as fabrics, the compositions will preferably comprise less than about 1%, preferably less than about 0.9%, more preferably less than about 0.5%, and even more preferably less than about 0.2%, by weight of the composition, of microcapsules. If the level of microcapsules is too high, the compositions may leave a visible residue on the surface being treated. In addition, if the surface is fabric and the level of microcapsules is too high, the fabric appearance may be altered. Furthermore, if the active material is perfume and the level of microcapsules is too high, the initial perfume "burst" when the product is sprayed onto the surface may be unpleasant to the consumer, since the force of the spray tends to rupture some of the microcapsules.

A variety of processes known in the art can be used to make the microcapsules herein. Examples of processes for making microcapsules are described in U.S. Patent Nos. 2,800,458; 3,159,585; 3,516,846; 3,516,941; 3,533,958; 3,697,437; 3,778,383; 3,888,689; 3,965,033; 3,996,156; 4,010,038; 4,016,098; 4,087,376; 4,089,802; 4,100,103; 4,251,386; 4,269,729; 4,303,548; 4,460,722; and 4,610,927; UK Patent Nos. 1,156,725; 1,483,542; 2,041,319 and 2,048,206; and Benita, Simon (ed.), MICROENCAPSULATION: METHODS AND INDUSTRIAL APPLICATIONS (Marcel Dekker, Inc. 1996).

The active material can be a wide variety of materials in which one would want to deliver in a controlled-release manner onto the surfaces being treated with the present compositions or into the environment surrounding the surfaces. Non-limiting examples of active materials include perfumes, flavoring agents, fungicide, brighteners, antistatic agents, wrinkle control agents, fabric softener actives, hard surface cleaning actives, skin and/or hair conditioning agents, antimicrobial actives, UV protection agents, insect repellants, animal/vermin repellants, flame retardants, and the like.

In a preferred embodiment, the active material is a perfume, in which case the microcapsules containing perfume provide a controlled-release scent onto the surface being treated or into the environment surrounding the surface. In this case, the perfume can be comprised of a number of perfume raw materials known in the art, such as essential oils, botanical extracts, synthetic perfume materials, and the like.

In general, the active material is contained in the microcapsule at a level of from about 1% to about 99%, preferably from about 10% to about 95%, and more preferably from about 30% to about 90%, by weight of the total microcapsule. The encapsulated odor control agent, if present may be contained in microcapsules at the same range of levels. Of course if both active material and an odor control agent are contained in the same microcapsule, the total percentage of these components will never exceed 100%. The weight of the total microcapsule includes the weight of the shell of the microcapsule plus the weight of the material inside the microcapsule.

Microcapsules containing an active material, preferably perfume, suitable for use in the present compositions are described in detail in, e.g., U.S. Patent Nos. 3,888,689; 4,520,142; 5,126,061; and 5,591,146.

ODOR CONTROL AGENTS

In general, the present malodor-controlling compositions will comprise one or more odor control agent(s) at a level of from about 0.001% to about 99.99%, preferably from about 0.002% to about 99.9%, and more preferably from about 0.005% to about 99%, by weight of the malodor-controlling composition. When the compositions are aqueous liquid compositions (especially non-aerosol compositions) to be sprayed onto surfaces, such as fabrics, the compositions will

preferably comprise less than about 20%, preferably less than about 10%, more preferably less than about 5%, by weight of the composition, of odor control agent. The odor control agent serves to reduce or remove malodor from the surfaces or objects being treated with the present compositions. The odor control agent is preferably selected from the group consisting of: uncomplexed cyclodextrin; odor blockers; reactive aldehydes; flavanoids; zeolites; activated carbon; and mixtures thereof.

Uncomplexed Cyclodextrin

As used herein, the term "uncomplexed cyclodextrin" includes any of the known cyclodextrins in uncomplexed form such as unsubstituted cyclodextrins containing from six to twelve glucose units, especially, alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin and/or their derivatives and/or mixtures thereof. The alpha-cyclodextrin consists of six glucose units, the beta-cyclodextrin consists of seven glucose units, and the gamma-cyclodextrin consists of eight glucose units arranged in donut-shaped rings. The specific coupling and conformation of the glucose units give the cyclodextrins a rigid, conical molecular structures with hollow interiors of specific volumes. The "lining" of each internal cavity is formed by hydrogen atoms and glycosidic bridging oxygen atoms; therefore, this surface is fairly hydrophobic. The unique shape and physical-chemical properties of the cavity enable the cyclodextrin molecules to absorb (form inclusion complexes with) organic molecules or parts of organic molecules which can fit into the cavity. Many odorous molecules can fit into the cavity including many malodorous molecules and perfume molecules. Therefore, cyclodextrins, and especially mixtures of cyclodextrins with different size cavities, can be used to control odors caused by a broad spectrum of organic odoriferous materials, which may, or may not, contain reactive functional groups. The complexation between cyclodextrin and odorous molecules occurs rapidly in the presence of water. However, the extent of the complex formation also depends on the polarity of the absorbed molecules. In an aqueous solution, strongly hydrophilic molecules (those which are highly water-soluble) are only partially absorbed, if at all. Therefore, cyclodextrin does not complex effectively with some very low molecular weight organic amines and acids when they are present at low levels on surfaces.

The cavities within the cyclodextrin in the deodorizing composition of the present invention should remain essentially unfilled (the cyclodextrin remains uncomplexed) while in solution, in order to allow the cyclodextrin to absorb various odor molecules when the solution is applied to a surface. Non-derivatised (normal) beta-cyclodextrin can be present at a level up to its solubility limit of about 1.85% (about 1.85g in 100 grams of water) under the conditions of use at room temperature.

Preferably, the cyclodextrin used in the present invention is highly water-soluble such as, alpha-cyclodextrin and/or derivatives thereof, gamma-cyclodextrin and/or derivatives thereof, derivatised beta-cyclodextrins, and/or mixtures thereof. The derivatives of cyclodextrin consist mainly of molecules wherein some of the OH groups are converted to OR groups. Cyclodextrin derivatives include, e.g., those with short chain alkyl groups such as methylated cyclodextrins, and ethylated cyclodextrins, wherein R is a methyl or an ethyl group; those with hydroxyalkyl substituted groups, such as hydroxypropyl cyclodextrins and/or hydroxyethyl cyclodextrins, wherein R is a $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_3$ or a $-\text{CH}_2\text{CH}_2-\text{OH}$ group; branched cyclodextrins such as maltose-bonded cyclodextrins; cationic cyclodextrins such as those containing 2-hydroxy-3-(dimethylamino)propyl ether, wherein R is $\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{N}(\text{CH}_3)_2$ which is cationic at low pH; quaternary ammonium, e.g., 2-hydroxy-3-(trimethylammonio)propyl ether chloride groups, wherein R is $\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{N}^+(\text{CH}_3)_3\text{Cl}^-$; anionic cyclodextrins such as carboxymethyl cyclodextrins, cyclodextrin sulfates, and cyclodextrin succinylates; amphoteric cyclodextrins such as carboxymethyl/quaternary ammonium cyclodextrins; cyclodextrins wherein at least one glucopyranose unit has a 3-6-anhydro-cyclomalto structure, e.g., the mono-3-6-anhydrocyclodextrins, as disclosed in "Optimal Performances with Minimal Chemical Modification of Cyclodextrins", F. Diedaini-Pilard and B. Perly, The 7th International Cyclodextrin Symposium Abstracts, April 1994, p. 49; and mixtures thereof. Other cyclodextrin derivatives are disclosed in U.S. Pat. Nos. 3,426,011, Parmerter et al., issued Feb. 4, 1969; 3,453,257; 3,453,258; 3,453,259; and 3,453,260, all in the names of Parmerter et al., and all issued July 1, 1969; 3,459,731, Gramera et al., issued Aug. 5, 1969; 3,553,191, Parmerter et al., issued Jan. 5, 1971; 3,565,887, Parmerter et al., issued Feb. 23, 1971; 4,535,152, Szejtli et al., issued Aug. 13, 1985; 4,616,008, Hirai et al., issued Oct. 7, 1986; 4,678,598, Ogino et al., issued Jul. 7, 1987; 4,638,058, Brandt et al., issued Jan. 20, 1987; and 4,746,734, Tsuchiyama et al., issued May 24, 1988. Further cyclodextrin derivatives suitable herein include those disclosed in V. T. D'Souza and K. B. Lipkowitz, CHEMICAL REVIEWS: CYCLODEXTRINS, Vol. 98, No. 5 (American Chemical Society, July/August 1998).

Highly water-soluble cyclodextrins are those having water solubility of at least about 10 g in 100 ml of water at room temperature, preferably at least about 20 g in 100 ml of water, more preferably at least about 25 g in 100 ml of water at room temperature. The availability of solubilized, uncomplexed cyclodextrins is essential for effective and efficient odor control performance. Solubilized, water-soluble cyclodextrin can exhibit more efficient odor control performance than non-water-soluble cyclodextrin when deposited onto surfaces, especially carpeted surfaces.

Examples of preferred water-soluble cyclodextrin derivatives suitable for use herein are hydroxypropyl alpha-cyclodextrin, methylated alpha-cyclodextrin, methylated beta-cyclodextrin, hydroxyethyl beta-cyclodextrin, and hydroxypropyl beta-cyclodextrin. Hydroxyalkyl cyclodextrin derivatives preferably have a degree of substitution of from about 1 to about 14, more preferably from about 1.5 to about 7, wherein the total number of OR groups per cyclodextrin is defined as the degree of substitution. Methylated cyclodextrin derivatives typically have a degree of substitution of from about 1 to about 18, preferably from about 3 to about 16. A known methylated beta-cyclodextrin is heptakis-2,6-di-O-methyl- β -cyclodextrin, commonly known as DIMEB, in which each glucose unit has about 2 methyl groups with a degree of substitution of about 14. A preferred, more commercially available, methylated beta-cyclodextrin is a randomly methylated beta-cyclodextrin, commonly known as RAMEB, having different degrees of substitution, normally of about 12.6. RAMEB is more preferred than DIMEB, since DIMEB affects the surface activity of the preferred surfactants more than RAMEB. The preferred cyclodextrins are available, e.g., from Cerestar USA, Inc. and Wacker Chemicals (USA), Inc.

It is also preferable to use a mixture of cyclodextrins. Such mixtures absorb odors more broadly by complexing with a wider range of odoriferous molecules having a wider range of molecular sizes. Preferably at least a portion of the cyclodextrin is alpha-cyclodextrin and its derivatives thereof, gamma-cyclodextrin and its derivatives thereof, and/or derivatised beta-cyclodextrin, more preferably a mixture of alpha-cyclodextrin, or an alpha-cyclodextrin derivative, and derivatised beta-cyclodextrin, even more preferably a mixture of derivatised alpha-cyclodextrin and derivatised beta-cyclodextrin, most preferably a mixture of hydroxypropyl alpha-cyclodextrin and hydroxypropyl beta-cyclodextrin, and/or a mixture of methylated alpha-cyclodextrin and methylated beta-cyclodextrin.

Since cyclodextrin can be a prime breeding ground for certain microorganisms, especially when in aqueous compositions, it is preferable to include a water-soluble preservative, as described *infra*, which is effective for inhibiting and/or regulating microbial growth, to increase storage stability of aqueous odor-absorbing solutions containing water-soluble cyclodextrin.

Odor Blockers

"Odor blockers" can be used as an odor control agent to mitigate the effects of malodors. In order to be effective, the odor blockers normally have to be present at all times. If the odor blocker evaporates before the source of the odor is gone, it is less likely to control the odor. Also, the odor blockers can tend to adversely affect aesthetics by blocking desirable odors like perfumes.

Non-limiting examples of odor blockers suitable as odor control agents in the present compositions include 4-cyclohexyl-4-methyl-2-pentanone, 4-ethylcyclohexyl methyl ketone, 4-isopropylcyclohexyl methyl ketone, cyclohexyl methyl ketone, 3-methylcyclohexyl methyl ketone, 4-tert.-butylcyclohexyl methyl ketone, 2-methyl-4-tert.butylcyclohexyl methyl ketone, 2-methyl-5-isopropylcyclohexyl methyl ketone, 4-methylcyclohexyl isopropyl ketone, 4-methylcyclohexyl sec.butyl ketone, 4-methylcyclohexyl isobutyl ketone, 2,4-dimethylcyclohexyl methyl ketone, 2,3-dimethylcyclohexyl methyl ketone, 2,2-dimethylcyclohexyl methyl ketone, 3,3-dimethylcyclohexyl methyl ketone, 4,4-dimethylcyclohexyl methyl ketone, 3,3,5-trimethylcyclohexyl methyl ketone, 2,2,6-trimethylcyclohexyl methyl ketone, 1-cyclohexyl-1-ethyl formate, 1-cyclohexyl-1-ethyl acetate, 1-cyclohexyl-1-ethyl propionate, 1-cyclohexyl-1-ethyl isobutyrate, 1-cyclohexyl-1-ethyl n-butyrate, 1-cyclohexyl-1-propyl acetate, 1-cyclohexyl-1-propyl n-butyrate, 1-cyclohexyl-2-methyl-1-propyl acetate, 2-cyclohexyl-2-propyl acetate, 2-cyclohexyl-2-propyl propionate, 2-cyclohexyl-2-propyl isobutyrate, 2-cyclohexyl-2-propyl n-butyrate, 5,5-dimethyl-1,3-cyclohexanedione (dimedone), 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid), spiro-[4.5]-6,10-dioxo-7,9-dioxodecane, spiro-[5.5]-1,5-dioxo-2,4-dioxoundecane, 2,2-hydroxymethyl-1,3-dioxane-4,6-dione and 1,3-cyclohexadione. Odor blockers are disclosed in more detail in U.S. Patent Nos. 4,009,253; 4,187,251; 4,719,105; 5,441,727; and 5,861,371.

Reactive Aldehydes

As an optional odor control agent, reactive aldehydes can be used as an odor control agent to mitigate the effects of malodors. Non-limiting examples of suitable reactive aldehydes include Class I aldehydes, Class II aldehydes, and mixtures thereof. Non-limiting examples of Class I aldehydes include anisic aldehyde, o-allyl-vanillin, benzaldehyde, cuminic aldehyde, ethyl-aubepin, ethyl-vanillin, heliotropin, tolyl aldehyde, and vanillin. Non-limiting examples of Class II aldehydes include 3-(4'-tert.butylphenyl)propanal, 2-methyl-3-(4'-tert.butylphenyl)propanal, 2-methyl-3-(4'-isopropylphenyl)propanal, 2,2-dimethyl-3-(4-ethylphenyl)propanal, cinnamic aldehyde, α -amyl-cinnamic aldehyde, and α -hexyl-cinnamic aldehyde. These reactive aldehydes are described in more detail in U.S. Patent No. 5,676,163.

Reactive aldehydes, when used, can include a combination of at least two aldehydes, with one aldehyde being selected from acyclic aliphatic aldehydes, non-terpenic aliphatic aldehydes, non-terpenic alicyclic aldehydes, terpenic aldehydes, aliphatic aldehydes substituted by an aromatic group and bifunctional aldehydes; and the second aldehyde being selected from aldehydes possessing an unsaturation alpha to the aldehyde function conjugated with an aromatic ring, and aldehydes in which the aldehyde group is on an aromatic ring. This combination of at

least two aldehydes is described in more detail in International Patent Application Pub. No. WO 00/49120.

As used herein, the term "reactive aldehydes" further encompasses deodorizing materials that are the reaction products of (i) an aldehyde with an alcohol, (ii) a ketone with an alcohol, or (iii) an aldehyde with the same or different aldehydes. Such deodorizing materials can be: (a) an acetal or hemiacetal produced by means of reacting an aldehyde with a carbinol; (b) a ketal or hemiketal produced by means of reacting a ketone with a carbinol; (c) a cyclic triacetal or a mixed cyclic triacetal of at least two aldehydes, or a mixture of any of these acetals, hemiacetals, ketals, hemiketals, or cyclic triacetals. These deodorizing perfume materials are described in more detail in International Patent Application Pub. No. WO 01/07095.

Flavanoids

Flavanoids can also be used as an odor control agent. Flavanoids are compounds based on the C₆ C₃ C₆ flavan skeleton. Flavanoids can be found in typical essential oils. Such oils include essential oil extracted by dry distillation from needle leaf trees and grasses such as cedar, Japanese cypress, eucalyptus, Japanese red pine, dandelion, low striped bamboo and cranesbill and can contain terpenic material such as alpha-pinene, beta-pinene, myrcene, phencone and camphene. Also included are extracts from tea leaf. Descriptions of such materials can be found in JP 02284997 and JP 04030855.

Metallic Salts

The odor control agent of the present invention can include metallic salts for malodor control benefits. The metallic salts are selected from the group consisting of copper salts, zinc salts, and mixtures thereof.

The preferred zinc salts possess malodor control abilities. Zinc has been used most often for its ability to ameliorate malodor, e.g., in mouth wash products, as disclosed in U.S. Patent Nos. 4,325,939 and 4,469,674. Highly-ionized and soluble zinc salts such as zinc chloride, provide the best source of zinc ions. Preferred zinc salts are selected from the group consisting of zinc borate, zinc caprylate, zinc chloride, zinc ricinoleate, zinc sulfate heptahydrate, zinc undecylenate, and mixtures thereof.

Preferably the metallic salts are water-soluble zinc salts, copper salts or mixtures thereof, and more preferably zinc salts, especially ZnCl₂. These salts are preferably present in the present invention as an odor control agent primarily to absorb amine and sulfur-containing compounds. Low molecular weight sulfur-containing materials, e.g., sulfide and mercaptans, are components of many types of malodors, e.g., food odors (garlic, onion), body/perspiration odor, breath odor, etc. Low molecular weight amines are also components of many malodors, e.g., food odors, body odors, urine, etc.

Zinc salts, when used, can be combined with an anionic surfactant having the formula $R-(O-CH_2-CH_2)_x-O-CH_2COO^-$, wherein R is a fatty alcohol substituent or an alkylaryl substituent and X is at least 2. Such anionic surfactants can act as a control release agent for the zinc salts to improve the malodor control properties of the composition. This combination of zinc salts and anionic surfactant is described in more detail in U.S. Patent No. 6,358,469.

Zinc salts, when used, can also be combined with carbonate and/or bicarbonate to improve the malodor control properties of the composition. When zinc salts are combined with carbonate and/or bicarbonate, the composition preferably further comprises a stabilizing anion selected from phosphates having more than one $-(P=O)-$ group and organic acids having more than one acid functionality. This combination of zinc salts, carbonate and/or bicarbonate, and stabilizing anions is described in more detail in U.S. Patent No. 6,015,547.

Copper salts possess some malodor control abilities. See U.S. Patent No. 3,172,817, Leupold, et al., which discloses deodorizing compositions for treating disposable articles, comprising at least slightly water-soluble salts of acylacetone, including copper salts and zinc salts.

When metallic salts are added to the composition of the present invention as an odor control agent, they are typically present at a level of from about 0.001% to an effective amount to provide a saturated salt solution, preferably from about 0.002% to about 25%, more preferably from about 0.003% to about 8%, still more preferably from about 0.1% to about 5% by weight of the composition.

Zeolites

The odor control agents herein can also be zeolites. A preferred class of zeolites is characterized as "intermediate" silicate/aluminate zeolites. The intermediate zeolites are characterized by SiO_2/AlO_2 molar ratios of less than about 10. Preferably the molar ratio of SiO_2/AlO_2 ranges from about 2 to about 10. The intermediate zeolites can have an advantage over the "high" zeolites. The intermediate zeolites have a higher affinity for amine-type odors, they are more weight efficient for odor absorption because they have a larger surface area, and they are more moisture tolerant and retain more of their odor absorbing capacity in water than the high zeolites. A wide variety of intermediate zeolites suitable for use herein are commercially available as Valfor® CP301-68, Valfor® 300-63, Valfor® CP300-35, and Valfor® CP300-56, available from PQ Corporation, and the CBV100® series of zeolites from Conteka.

Zeolite materials marketed under the trade name Abscents® and Smellrite®, available from The Union Carbide Corporation and UOP are also preferred. Such materials are preferred over the intermediate zeolites for control of sulfur-containing odors, e.g., thiols, mercaptans.

When zeolites are used as odor control agents in compositions that are to be sprayed onto surfaces, the zeolite material preferably has a particle size of less than about 10 microns and is present in the composition at a level of less than about 1% by weight of the composition.

Activated Carbon

Activated carbon is another suitable odor control agent for incorporation in the present compositions. The carbon material suitable for use in the present invention is the material well known in commercial practice as an absorbent for organic molecules and/or for air purification purposes. Often, such carbon material is referred to as "activated" carbon or "activated" charcoal. Such carbon is available from commercial sources under such trade names as; Calgon-Type CPG[®]; Type PCB[®]; Type SGL[®]; Type CAL[®]; and Type OL[®].

When activated carbon is used as an odor control agent in compositions that are to be sprayed onto surfaces, the activated carbon preferably has a particle size of less than about 10 microns and is present in the composition at a level of less than about 1% by weight of the composition.

To the extent any material described herein as an odor control agent might also be classified as another component described herein, for purposes of the present invention, such material shall be classified as an odor control agent.

AQUEOUS CARRIER

The aqueous carrier of the present invention comprises water. The water which is used can be distilled, deionized, or tap water. Water not only serves as the liquid carrier for the microcapsules, but it also facilitates the reaction between the odor control agents and any unwanted molecules on surfaces, such as malodorous molecules that are on inanimate surfaces such as fabric, when the surface is treated. It has been found that the intensity of unwanted malodorous molecules generated by some polar, low molecular weight organic amines, acids, and mercaptans is reduced when the malodor-contaminated surfaces are treated with an aqueous solution. It is believed that water solubilizes and depresses the vapor pressure of these polar, low molecular weight organic molecules, thus reducing their odor intensity.

The level of aqueous carrier in the present compositions can vary dependent upon the use of the composition. In general, the level of aqueous carrier in the present compositions can be from about 0.1% to about 99.9%. In compositions designed to be sprayed from manually or non-manually operated spray dispensers, the level of aqueous carrier is preferably high, for example, at a level of at least about 80%, preferably at least about 85%, more preferably at least about 90%, and even more preferably at least about 95%, by weight of the composition.

OPTIONAL INGREDIENTS

The present compositions can further comprise a wide variety of optional ingredients, such as dispersants, solvents, aerosol propellants, surfactants, free perfume, preservatives / antimicrobial actives, wrinkle control agents, and the like.

Dispersants

The present compositions optionally, but preferably, further comprise a dispersant. A dispersant can be important to suspend the microcapsules in the composition to prevent the microcapsules from falling out of solution. Thus a dispersant can be important in achieving a composition that is stable.

When the present compositions are designed to be sprayed from a spray dispenser, it can be important to select a level and type of dispersant that provides enough suspension for microcapsule particles, but at the same time is easily sprayable as a fine mist. Some dispersants are capable of suspending particles, but result in compositions having viscosities that are too high to be easily sprayable as a fine mist.

In this respect, the level and type of dispersant is preferably selected to provide a non-Newtonian viscosity property. The resulting malodor-controlling compositions thus will preferably have a difference of viscosity at shear rate 1 sec^{-1} and at 10 sec^{-1} of at least about 0.1 centipoise, preferably at least about 0.5 centipoise, and more preferably at least about 1 centipoise. In this regard, the compositions herein are preferably shear-thinning. The resulting malodor-controlling compositions are capable of adequately suspending particles therein (e.g. microcapsules) while being easily sprayable from a spray dispenser.

The preferred dispersants herein provide a shear-thinning composition having a weak gel formation matrix, in which polymeric or non-polymeric ingredients interact with each other and form hydrogen and/or hydrophobic bonding. Some functional groups on the molecules have electrostatic repulsive forces that can prevent coagulation of the particles in the composition. The weakly formed gel matrix resulting from the preferred dispersants herein is capable of suspending micron size particles, such as microcapsules, in the composition matrix.

When present, dispersants are typically included at a level of from about 0.001% to about 10%, preferably from about 0.005% to about 5%, and more preferably from about 0.01% to about 1%, by weight of the composition. If it is desired to keep the viscosity of the present compositions relatively low, e.g. if the compositions are to be sprayed onto surfaces (e.g. fabrics) via a spray dispenser, the dispersant is preferably included at a level of less than about 1%, more preferably less than about 0.9%, and even more preferably less than about 0.8%, by weight of the composition. If the level of dispersant is too high, the composition may leave a visible residue on

the treated surfaces. If the composition is to be sprayed on fabrics and the level of dispersant is too high, the composition may undesirably alter the fabric feel or softness.

The dispersants herein can be selected from materials such as pectine, alginate, arabinogalactan, carageenan, gellan gum, xanthum gum, guar gum, acrylates/acrylic polymers, water-swellaible clays, fumed silicas, acrylate/aminoacrylate copolymers, and mixtures thereof. Preferred dispersants herein include those selected from the group consisting of acrylate/acrylic polymers, gellan gum, fumed silicas, acrylate/aminoacrylate copolymers, water-swellaible clays, and mixtures thereof.

Acrylate/acrylic polymers include acrylic emulsion terpolymers. These types of dispersants are typically alkali activated. Suitable alkali activated acrylate/acrylic polymers are described in detail in U.S. Patent Nos. 5,990,233 and 5,840,789. Such alkali activated acrylate/acrylic polymer dispersants are available from Alco Chemical under the trade name ALCOGUM® SL series.

Gellan gum is a heteropolysaccharide prepared by fermentation of *Pseudomonas elodea* ATCC 31461. Gellan gum is available from CP Kelco U.S., Inc. under various names, including KELCOGEL®, KELCOGEL® LT100, KELCOGEL® AFT, KELCOGEL® AF, KELCOGEL® PC, and KELCOGEL® F. Processes for preparing gellan gum are described in U.S. Patent No. 4,326,052 (Kang et al), issued Apr. 20, 1982; U.S. Patent No. 4,326,053 (Kang et al), issued Apr. 20, 1982; U.S. Patent No. 4,377,636 (Kang et al), issued Mar. 22, 1983; and U.S. Patent No. 4,385,123 (Kang et al), issued May 24, 1983.

Fumed silicas are a colloidal form of silica made by combustion of silicon tetrachloride in hydrogen-oxygen furnaces. Fumed silicas are known by the chemical name silicium dioxide. Fumed silicas suitable in the present compositions are available from Degussa AG under the tradename AEROSIL®. A preferred fumed silica is AEROSIL® 200 (available from Degussa AG), which is a hydrophilic fumed silica having a specific surface area of about 200 m²/gram.

Acrylate/aminoacrylate copolymers are typically aqueous dispersions of an amine functional acrylic polymer rheology modifier. These types of dispersants are typically acid activated, as compared to acrylate/acrylic polymer dispersants described hereinbefore which are typically alkali activated. Acrylate/aminoacrylate copolymers are available from Alco Chemical under the trade name ALCOGUM® L-500 series. Preferred acrylate/aminoacrylate copolymers are ALCOGUM® L-511 and ALCOGUM® L-520 which are aqueous dispersions of amine functional acrylic polymers available from Alco Chemical.

Water-swellaible clays include hectorites and synthetic layered silicates. Synthetic layered silicates are available from Southern Clay Products, Inc. under the trade name LAPONITE®. These synthetic layered silicates are layered hydrous magnesium silicates, in which magnesium

ions, partially replaced by suitable monovalent ions such as lithium, sodium, potassium and/or vacancies, are octahedrally coordinated to oxygen and/or hydroxyl ions, some of which may be replaced by fluorine ions, forming the central octahedral sheet, the octahedral sheet being sandwiched between two tetrahedral sheets of silicon ions, tetrahedrally coordinated to oxygen. Preferred synthetic layered silicates include LAPONITE® RD and LAPONITE® RDS available from Southern Clay Products, Inc. Hectorites are available from Rheox, Inc. under the trade name BENTONE®. These hectorites are prepared by reacting bentonite in a cation exchange system with an amine. Preferred hectorites include BENTONE® LT and BENTONE® AD available from Rheox, Inc.

Solvents

The present compositions can further comprise optional solvents. Solvents can help to provide compositions that dry more quickly after being applied to surfaces, versus compositions that do not contain solvent. Where it is desirable to have a composition that quickly dries after being applied to a surface, the present compositions preferably further comprise solvents. Suitable solvents herein include monohydric and polyhydric alcohols. Monohydric alcohols useful as solvents in the present composition include ethanol, n-propanol, isopropanol, mixtures thereof, and the like. Polyhydric alcohols useful as solvents in the present composition include glycols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, glycerine, mixtures thereof, and the like. Other suitable solvents include water-miscible ethers, water-miscible glycol ethers, and propylene glycol monomethyl ether acetate. Non-limiting examples of water-miscible ethers include diethylene glycol diethylether, diethyleneglycol dimethylether, propylene glycol dimethylether, and mixtures thereof. Non-limiting examples of water-miscible glycol ethers include propylene glycol monomethylether, propylene glycol monoethylether, propylene glycol monopropylether, propylene glycol monobutylether, ethylene glycol monobutylether, dipropylene glycol monomethylether, diethyleneglycol monobutylether, and mixtures thereof.

When present, the level of solvent in the present compositions is generally from about 0.1% to about 99.9%, preferably from about 0.5% to about 99%, and more preferably from about 1% to about 90%. If the compositions are spray compositions (especially non-aerosol), the level of alcohol is preferably less than about 35%, more preferably less than about 20%, and even more preferably less than about 10%, by weight of the composition.

Aerosol Propellants

Wherein the present compositions are in the form of an aerosol spray composition, the compositions further comprise an aerosol propellant. Non-limiting examples of suitable aerosol propellants for aerosol compositions herein include aliphatic hydrocarbons such as butane,

isobutane, and propane; low molecular weight halogenated hydrocarbons (preferably chlorinated and/or fluorinated hydrocarbons) such as chlorodifluoromethane; dissolvable gases such as carbon dioxide; nitrogen gas; compressed air; and other materials well known in the art.

When present, aerosol propellants are typically incorporated in the present compositions at a level of from about 2% to about 60%, preferably from about 3% to about 50%, by weight of the composition.

Aerosol propellants especially suitable for incorporation in the present compositions are described in detail in U.S. Patent No. 4,520,142.

Surfactants

To improve the ability of the present compositions to "wet" the surfaces being treated (i.e. improve the ability of the composition to spread across the surface), the compositions preferably further comprise optional surfactants. Preferably, the compositions comprise a surfactant, or mixtures of surfactants, at a level of from about 0.001% to about 90%, preferably from about 0.01% to about 80%, and more preferably from about 0.05% to about 70%, by weight of the composition. If the composition is intended to be sprayed onto the surface via a spray dispenser, the compositions preferably include optional surfactants at a level of less than about 5%, preferably less than about 3%, and more preferably less than about 1%, by weight of the composition.

Surfactants are generally well-known in the detergent art. Surfactants which are suitable in the compositions of the present invention include anionic, nonionic, cationic, amphoteric, zwitterionic, and mixtures of the above types.

Preferred surfactants are described in detail in U.S. Patent Application Pub. No. US 2002/0011584 A1.

Anionic Surfactants

Anionic surfactants can optionally be incorporated in the present compositions. Many suitable nonlimiting examples from the class of anionic surfactants can be found in Surfactants and Interfacial Phenomena, 2nd Ed., Milton J. Rosen, 1989, John Wiley & Sons, Inc., pp. 7-16. Additional suitable nonlimiting examples of anionic surfactants can be found in *Handbook of Surfactants*, M.R. Porter, 1991, Blackie & Son Ltd, pp. 54-115 and references therein.

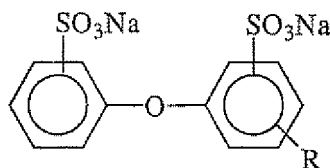
Structurally, suitable anionic surfactants contain at least one hydrophobic moiety and at least one hydrophilic moiety. The surfactant can contain multiple hydrophobic moieties and/or multiple hydrophilic moieties, but preferably less than or equal to about 2 hydrophobic moieties and less than or equal to about 3 hydrophilic moieties. The hydrophobic moiety is typically comprised of hydrocarbons either as an alkyl group or an alkyl-aryl group. Alkyl groups typically contain from about 6 to about 22 carbons, preferably about 10 to about 18 carbons, and more

preferably from about 12 to about 16 carbons; aryl groups typically contain alkyl groups containing from about 4 to about 6 carbons. Each alkyl group can be a branched or linear chain and is either saturated or unsaturated. A typical aryl group is benzene. Some typical hydrophilic groups for anionic surfactants include but are not limited to $-\text{CO}_2^-$, $-\text{OSO}_3^-$, $-\text{SO}_3^-$, $-(\text{OR}_1)_x-\text{CO}_2^-$, $-(\text{OR}_1)_x-\text{OSO}_3^-$, $-(\text{OR}_1)_x-\text{SO}_3^-$ where x is being less than about 10 and preferably less than about 5. Some nonlimiting examples of suitable surfactants includes, Stepanol® WAC, Biosoft® 40 (Stepan Co., Northfield, IL).

Anionic surfactants can also be created by sulfating or sulfonating animal or vegetable based oils. An example of these type of surfactants include sulfated canola oil and sulfated castor oil (Freedom SCO-75) available from the Freedom Chemical Co., Charlotte NC (owned by BF Goodrich).

Non-limiting examples of suitable anionic surfactants include salts of C_8 - C_{22} alkyl fatty acids; C_{10} - C_{14} alkylbenzene sulfonates; C_{10} - C_{22} alkene sulfonates; C_{10} - C_{22} alkyl ether sulfonates; C_{10} - C_{22} alkyl sulfates; C_4 - C_{10} dialkyl sulfosuccinates; C_{10} - C_{22} acyl methionates; alkyl diphenyloxide sulfonates; alkyl naphthalene sulfonates; 2-acetamido hexadecane sulfonates; alkyl glyceryl ether sulfonates; and N-alkyl substituted succinates. Anionic surfactants which are water-soluble alkylbenzene sulfonate salts of organic sulfur-reaction products are described in U.S. Patent Nos. 2,220,099 and 2,477,383. Especially valuable are linear straight-chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C_{11} - C_{13} LAS. Other anionic surfactants are described in U.S. Patent No. 6,358,469, which are preferred when the present compositions comprise zinc salts in combination with carbonate and/or bicarbonate.

When the present compositions comprise uncomplexed cyclodextrin as an odor control agent, the anionic surfactant is preferably cyclodextrin-compatible, meaning that the surfactant does not tend to form complexes with cyclodextrin. Nonlimiting examples of cyclodextrin-compatible anionic surfactants are the alkyldiphenyl oxide disulfonates, having the general formula:



wherein R is an alkyl group. Examples of this type of surfactants are available from the Dow Chemical Company under the trade name Dowfax® wherein R is a linear or branched C_6 - C_{16}

alkyl group. An example of these cyclodextrin-compatible anionic surfactant is Dowfax 3B2 with R being approximately a linear C₁₀ group.

Nonionic Surfactants

The present compositions can optionally comprise nonionic surfactants, which are the preferred surfactants in the present compositions. Non-limiting examples of suitable nonionic surfactants include alkyl ethoxylated surfactants, block copolymer surfactants, castor oil surfactants, sorbitan ester surfactants, polyethoxylated fatty alcohol surfactants, glycerol mono-fatty acid ester surfactants, polyethylene glycol fatty acid ester surfactants, and mixtures thereof. These nonionic surfactants are described in more detail in U.S. Patent Application Pub. No. US 2002/0011584 A1.

Alkyl ethoxylated surfactants and castor oil surfactants are preferred nonionic surfactants. Castor oil surfactants include polyoxyethylene castor oil ethers or polyoxyethylene hardened castor oil ethers, which are either partially or fully hydrogenated. Preferred hydrogenated castor oil surfactants are commercially available from Nikko under the trade names HCO 40 and HCO 60 and from BASF under the trade names Cremphor™ RH 40, RH 60, and CO 60.

Cationic Surfactants

Cationic surfactants can also be incorporated in the present compositions. Cationic surfactants, when used in aqueous compositions to be sprayed on fabrics, can improve the ability of the composition to penetrate in between the fibers of the fabrics, which can lead to better performance in terms of reducing malodor and/or reducing the appearance of wrinkles on fabrics. Also, cationic surfactants can be useful to soften fabrics treated with the present compositions.

Suitable cationic surfactants include a wide variety of quaternary compounds. Preferred cationic surfactants are diester quaternary ammonium compounds ("DEQA"). These and other preferred quaternary compounds are described in detail in U.S. Patent Application Pub. No. US 2002/0011584 A1.

To the extent that a cationic surfactant acts as either an antimicrobial active or preservative, for purposes of the present invention, it shall be classified as an antimicrobial active / preservative, as described *infra*.

Amphoteric Surfactants

Amphoteric surfactants can also be used in the present compositions. Amphoteric surfactants, also called ampholytic surfactants, may be broadly defined as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and at least one contains an

anionic water-solubilizing group, e.g. carboxy, surfate, or sulfonate. Examples of suitable amphoteric surfactants can be found in U.S. Patent No. 3,929,678 at column 19, lines 18-35.

Zwitterionic Surfactants

The present compositions can optionally comprise zwitterionic surfactants. Zwitterionic surfactants may be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium, or tertiary sulfonium compounds.

Free Perfume

The stable, aqueous compositions of the present invention preferably comprise free perfume as an optional ingredient. As used herein, the term "free perfume" refers to perfume that is in the composition, but is not contained within microcapsules. Free perfume is desirable in the present compositions to provide a freshness impression on the surface being treated by the stable, aqueous compositions of the present invention. Free perfume is especially desired in compositions for treating fabrics, since it is important to provide a freshness impression on fabrics, especially clothing. Free perfume can be desirable to provide an immediate "burst" of perfume scent when the composition is applied to a surface, such as by spraying the composition on fabric, upholstered surfaces, or carpeting.

Suitable perfume materials for incorporation in the present compositions are disclosed, e.g., in U.S. Patent No. 5,939,060 issued August 17, 1999 to Trinh et al. at col. 2, line 38 to col. 7, line 53.

If free perfume is included in the stable, aqueous compositions of the present invention, it can be included at a wide variety of levels. Free perfume is typically at the level from about 0.0001 % to about 10 %, preferably from about 0.001 % to about 7%, and more preferably from about 0.01 % to about 5%, by weight of the composition.

Antimicrobial Actives / Preservatives

The present compositions can optionally further comprise antimicrobial actives / preservatives. As discussed hereinbefore, antimicrobial actives can constitute the active material contained in the microcapsules of the present compositions. In addition or alternatively, the present compositions can comprise free antimicrobial actives / preservatives, meaning antimicrobial actives / preservatives that are not contained within the microcapsules of the present compositions.

Antimicrobial actives / preservatives suitable for incorporation in the present compositions include many quaternary compounds, biguanide compounds, and other antimicrobial actives having antimicrobial efficacy. These materials can be incorporated in the present compositions in an effective amount to inhibit the growth of microorganisms in the

compositions themselves (i.e. act as a preservative) and/or to kill microorganisms on the surfaces being treated with the present compositions (i.e. act as an antimicrobial active).

Suitable antimicrobial actives / preservatives herein include quaternary compounds and biguanide compounds. Non-limiting examples of quaternary compounds include benzalkonium chlorides and/or substituted benzalkonium chlorides such as commercially available Barquat® (available from Lonza), Maquat® (available from Mason), Variquat® (available from Witco/Sherex), and Hyamine® (available from Lonza); di(C₆-C₁₄)alkyl di short chain (C₁₋₄ alkyl and/or hydroxyalkyl) quaternary such as Bardac® products of Lonza; N-(3-chloroallyl) hexaminium chlorides such as Dowicide® and Dowicil® available from Dow; benzethonium chloride such as Hyamine® from Rohm & Haas; methylbenzethonium chloride represented by Hyamine® 10X supplied by Rohm & Haas, cetylpyridinium chloride such as Cepacol chloride available from Merrell Labs; and diester quaternary ammonium compounds. Examples of preferred dialkyl quaternary compounds are di(C₈-C₁₂)dialkyl dimethyl ammonium chloride, such as didecyldimethylammonium chloride (Bardac® 22), and dioctyldimethylammonium chloride (Bardac® 2050). The quaternary compounds useful as cationic preservatives and/or antimicrobial agents herein are preferably selected from the group consisting of dialkyldimethylammonium chlorides, alkyldimethylbenzylammonium chlorides, dialkylmethylbenzylammonium chlorides, and mixtures thereof. Other preferred cationic antimicrobial actives useful herein include diisobutylphenoxyethoxyethyl dimethylbenzylammonium chloride (commercially available under the trade name Hyamine® 1622 from Rohm & Haas) and (methyl)diisobutylphenoxyethoxyethyl dimethylbenzylammonium chloride (i.e. methylbenzethonium chloride).

Non-limiting examples of biguanide compounds include 1,1'-hexamethylene bis(5-(p-chlorophenyl)biguanide), commonly known as chlorhexidine, and Cosmoci® CQ®, Vantocil® IB, including poly (hexamethylene biguanide) hydrochloride. Other useful antimicrobial actives include the bis-biguanide alkanes. Usable water soluble salts of the above are chlorides, bromides, sulfates, alkyl sulfonates such as methyl sulfonate and ethyl sulfonate, phenylsulfonates such as p-methylphenyl sulfonates, nitrates, acetates, gluconates, and the like.

Non-limiting examples of other suitable antimicrobial actives include Pyrrithiones (especially the zinc complex (ZPT)), Octopirox®, Dimethyldimethylol Hydantoin (Glydant®), Sodium Sulfite, Sodium Bisulfite, Imidazolidinyl Urea (Germall 115®), Diazolidinyl Urea (Germall II®), Benzyl Alcohol, 2-Bromo-2-nitropropane-1,3-diol (Bronopol®), Formalin (formaldehyde), Iodopropenyl Butylcarbamate (Polyphase P100®), Chloroacetamide, Methanamine, Methylidibromonitrile Glutaronitrile (1,2-Dibromo-2,4-dicyanobutane or

Tektamer[®]), Glutaraldehyde, 5-bromo-5-nitro-1,3-dioxane (Bronidox[®]), Phenethyl Alcohol, o-Phenylphenol/sodium o-phenylphenol, Sodium Hydroxymethylglycinate (Suttocide A[®]), Polymethoxy Bicyclic Oxazolidine (Nuosept C[®]), Dimethoxane, Thimersal, Dichlorobenzyl Alcohol, Captan, Chlorphenenesin, Dichlorophene, Chlorbutanol, Glyceryl Laurate, Halogenated Diphenyl Ethers, 2,4,4'-trichloro-2'-hydroxy-diphenyl ether (Triclosan[®] or TCS), 2,2'-dihydroxy-5,5'-dibromo-diphenyl ether, Phenolic Compounds (as described in U.S. Patent No. 6,190,674), Para-chloro-meta-xylene (PCMX), Chlorothymol, Phenoxyethanol, Phenoxyisopropanol, 5-Chloro-2-hydroxydiphenylmethane, Resorcinol and its Derivatives (as described in U.S. Patent No. 6,190,674), 5-Chloro 2,4-Dihydroxydiphenyl Methane, 4'-Chloro 2,4-Dihydroxydiphenyl Methane, 5-Bromo 2,4-Dihydroxydiphenyl Methane, 4'-Bromo 2,4-Dihydroxydiphenyl Methane, Bisphenolic Compounds (as described in U.S. Patent No. 6,190,674), Parabens (as described in U.S. Patent No. 6,190,674), Halogenated Carbanilides (as described in U.S. Patent No. 6,190,674), and mixtures thereof.

Antimicrobial actives, when present in the compositions of the present invention, are included at an effective amount to kill microorganisms on the surface being treated with the compositions, typically at a level of from about 0.001% to about 20%, preferably from about 0.01% to about 10%, and more preferably from about 0.05% to about 5%, by weight of the composition.

Wrinkle Control Agents

The present compositions can optionally further comprise a wrinkle control agent, wherein the wrinkle control agent helps to prevent and/or control wrinkles from forming in surfaces treated with the present compositions, especially fabrics. Wrinkle control agents useful herein include fiber lubricant, shape retention polymer, hydrophilic plasticizer, lithium salt, and mixtures thereof. Such wrinkle control agents are described in detail in U.S. Patent No. 6,001,343 issued December 14, 1999 to Trinh et al. Wrinkle control compositions that can be suitable as base compositions of the present invention that comprise microcapsules containing an active material, especially compositions that can be used in a cabinet-type or bag-type apparatus for conditioning garments, are also disclosed in co-pending U.S. Application Serial No. 09/674,224 filed April 27, 1998 by Hubesch et al. (which relates to WO 99/55950 published November 4, 1999); and co-pending U.S. Application Serial No. 09/673,600 filed April 27, 1998 by Woo et al. (which relates to WO 99/55816 published November 4, 1999).

Other additional optional ingredients can be included in the present compositions. Non-limiting examples of additional optional ingredients include brighteners, colorants, and the like.

The present compositions will typically have a pH of from about 2 to about 10, preferably from about 3 to about 9.5, and more preferably from about 3.5 to about 9. Depending on the

materials included in the composition, it can be desirable to adjust the pH of the composition to be acidic or alkaline. For example, if the composition contains an acid activated dispersant (e.g. acrylate/aminoacrylate copolymers such as ALCOGUM® L-511), the composition preferably has a pH of less than about 8, preferably less than about 7.5, and more preferably less than about 7. On the other hand, for example, if the composition contains an alkali activated dispersant (e.g. acrylate/acrylic polymers such as ALCOGUM® SL-70), the composition preferably has a pH of greater than about 4, preferably greater than about 5, and more preferably greater than about 5.5.

The compositions of the present invention can be in the form of aqueous liquids (e.g. fabric refreshers such as those described in U.S. Patent No. 6,146,621), aerosols (such as those described in U.S. Patent No. 4,520,142), gels (e.g. automatic dishwashing gels such as those described in U.S. Patent No. 5,384,061), pastes (e.g. toothpaste such as those described in U.S. Patent No. 4,701,319), lotions (e.g. skin lotions such as those described in U.S. Patent No. 5,968,258), powder detergent granules (e.g. laundry detergent compositions such as those described in U.S. Patent No. 5,338,476), shampoo/conditioners (such as those described in U.S. Patent No. 6,221,817), bar soaps (such as those described in U.S. Patent No. 5,254,281), and the like. The compositions can also be incorporated in substrates such as fabric softener dryer sheets (see, e.g., U.S. Patent No. 4,808,086), premoistened sheets for at-home dry cleaning processes (see, e.g., U.S. Patent No. 5,630,848), premoistened cleaning wipes (see, e.g., U.S. Patent No. 6,183,763), dry dusting sheets (see, e.g., U.S. Patent No. 5,525,397); and diapers (see, e.g., U.S. Patent No. 6,319,239). The compositions can also be incorporated in plug-in type air fresheners (such as those described in U.S. Patent No. 5,976,503). Preferably, the present compositions are aqueous liquids, especially those comprising relatively high amounts of water.

The preferred methods of the present invention relate to treating surfaces, preferably fabrics, with the stable, aqueous compositions of the present invention comprising the step of contacting the surface with the stable, aqueous composition. As used herein, the term "fabrics" is meant to encompass a variety of fabrics and articles composed of fabric and/or fibers, including but not limited to clothes, curtains, drapes, upholstered furniture, carpeting, bed linens, bath linens, tablecloths, sleeping bags, tents, car interior (e.g., car carpet, fabric car seats), and the like. The methods more specifically relate to reducing malodor impression on surfaces, especially fabrics, and/or reducing the appearance of wrinkles on fabrics. The surfaces are preferably treated by either spraying dilute aqueous compositions of the present invention onto the surfaces via a spray dispenser, or by adding the concentrated compositions of the present invention to, for example, a wash and/or rinse cycle in a typical laundry process.

A preferred method herein includes a method of reducing malodor impression on a surface (preferably fabrics) having malodor impression, the method comprising the step of contacting the surface with a stable, aqueous composition as described hereinbefore.

The composition for reducing malodor impression herein can be used by distributing, e.g., by placing the aqueous solution into a dispensing means, preferably a spray dispenser and spraying an effective amount onto the desired surface or article. An effective amount as defined herein means an amount sufficient to absorb odor to the point that it is not discernible by the human sense of smell yet not so much as to saturate or create a pool of liquid on said article or surface and so that when dry there is no visual deposit readily discernible. Distribution can be achieved by using a spray device, a roller, a pad, etc. For odor control, an effective amount, as defined herein, means an amount sufficient to absorb odor to effect a noticeable reduction in the perceived odor, preferably to the point that it is not discernible, by the human sense of smell.

The present invention encompasses the method of spraying an effective amount of the composition for reducing malodor onto household surfaces. Preferably said household surfaces are selected from the group consisting of countertops, cabinets, walls, floors, bathroom surfaces and kitchen surfaces.

Additional methods include, for example, adding the aqueous liquid composition to a steam iron and then using the steam iron to iron fabrics. Another method includes adding the aqueous liquid composition to a device for refreshing fabrics (such as that described in International Patent Application Pub. No. WO 02/14594).

When the present compositions include a wrinkle control agent, methods of controlling wrinkles in fabrics are encompassed by the present invention as described in detail in co-pending U.S. Patent Application Pub. No. US 2002/0011584 A1.

The compositions of the present invention can be packaged in a wide variety of packages well known in the art. When the present compositions are aqueous liquid compositions, the compositions are preferably packaged in a spray dispenser. Suitable spray dispensers can be manually operated or non-manually operated (e.g. battery-powered spray dispensers). Suitable spray dispensers are described in detail in U.S. Patent No. 6,284,231. When aerosol compositions are created, they are typically packaged in an aerosol spray dispenser, such as those described in U.S. Patent Nos. 3,436,772 and 3,600,325. Other suitable spray dispensers are described in more detail in U.S. Patent Nos. 4,082,223; 4,161,288; 4,434,917; 4,819,835; and 5,303,867.

The stable, aqueous compositions herein (especially concentrated compositions) can also be packaged in a bottle, especially a bottle that comprises a measuring closure. The measuring closure provides a convenient means to dispense the appropriate amount of the composition, especially when dispensing concentrated compositions into a wash and/or rinse solution

containing fabrics to be treated in a typical laundry process. The bottle also preferably comprises a drain-back spout, which permits the composition to be dispensed more easily and with less mess. Non-limiting examples of suitable bottles are described in detail in U.S. Patent No. 4,666,065 issued May 19, 1987 to Ohren; U.S. Patent No. 4,696,416 issued Sept. 29, 1987 to Muckenfuhs et al.; and U.S. Patent No. 4,981,239 issued Jan. 1, 1991 to Cappel et al.

The present compositions are made by mixing together the ingredients comprising the composition. A preferred process for making a composition of the present invention is described in Example 17.

The following are non-limiting examples of the present invention.

EXAMPLES

Component	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6	Ex 7	Ex 8
Water	To 100	To 100	To 100	To 100	To 100	To 100	To 100	To 100
Poly(oxymethyleneurea) microcapsules	0.1			0.1	0.1		0.2	
Poly(oxymethyleneurea) microcapsules containing odor control agents				0.1				
Poly(oxymethylenemelamine) microcapsules		0.15				0.1		
Gelatine microcapsules			0.2					
Polyurethane microcapsules								0.05
Acrylic Polymer	0.35	0.1	0.05			0.05		0.3
Water Swellable Clay						0.65	1.00	
Fumed Silica					0.5			
Gellan Gum				0.03				
Diethylene Glycol	0.1			0.38				
Polyalkyleneoxide modified polydimethylsiloxane	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Ethoxylated, Hydrogenated Castor Oil		0.1	0.2	0.1	0.2		0.1	0.05

Perfume	0.1	0.05		0.065	0.12	0.1	0.03	0.03
Hydroxypropyl beta-cyclodextrin	1.1	0.9		1.0		1.0		
Methylated beta-cyclodextrin			1.1		1.0		1.0	0.9
Ethanol	3	3	3	3	3	5	3	3
Citric Acid							0.07	

Component	Ex 9	Ex 10	Ex 11	Ex 12	Ex 13	Ex 14	Ex 15	Ex 16
Water	To 100	To 100	To 100	To 100	To 100	To 100	To 100	To 100
Poly(oxymethyleneurea) microcapsules	0.1				0.05		0.05	0.05
Poly(oxymethyleneurea) microcapsules containing odor control agents							0.10	0.15
Poly(oxymethylene melamine) microcapsules		0.15				0.07		
Gelatine microcapsules			0.05					
Polyurethane microcapsules				0.1				
Diethylene Glycol	0.25			0.1	0.1			
Polyalkyleneoxide modified polydimethylsiloxane	0.1	0.1	0.1	0.1	0.1	0.1		
Ethoxylated, Hydrogenated Castor Oil	0.1	0.1	0.2	0.05		0.1	0.1	0.1
Didecyl-dimethylammonium chloride	0.139	0.139	0.125		0.125			

Perfume	0.05	0.025	0.010	0.03	0.03	0.05	0.1	0.1
Hydroxypropyl beta-cyclodextrin					1.0		0.1	0.1
Methylated beta-cyclodextrin	1.00	1.00	1.00	1.1		1.0		
Ethanol	3	3	5	3	30	20	3	3
Acrylates/Aminoacrylates Copolymer	0.75	0.5	0.25	0.35	0.2		1.0	1.0
Citric Acid		0.1	0.2					
Lactic Acid	0.2	0.1		0.1	0.05		3	3
Aerosol Propellant					20	40		

For each composition in the above Examples 1-16, the pH of each composition is adjusted as needed between 3 and 11 with sodium hydroxide or hydrochloric acid. The microcapsules in each of the above Examples 1-16 contain from about 0.001% to about 99.9%, by weight of the total microcapsule, of an active material selected from the group consisting of perfumes, flavoring agents, fungicide, brighteners, antistatic agents, wrinkle control agents, fabric softener actives, hard surface cleaning actives, skin and/or hair conditioning agents, antimicrobial actives, UV protection agents, insect repellants, animal/vermin repellants, flame retardants, and mixtures thereof.

EXAMPLE 17

A one kilogram batch of a composition similar to that of Example 9 is made as follows. A mixer is used to blend the ingredients of the composition in a four liter beaker. The mixer has a 4" pitch blade and the mixing speed of the mixer is set at 150 RPM. The following ingredients are added to the four liter beaker in sequential order: 914.26 grams of water; 32.50 grams of ethanol; 1.11 grams of microcapsules containing perfume; 2.50 grams of diethylene glycol; 2.78 grams of Bardac[®] 2250; 1.00 grams of Silwet[®] L-7600; 1.00 grams of Cremophor[™] CO-60; 0.25 grams of free perfume. These ingredients are allowed to mix for 5 minutes. Then 19.88 grams of methylated beta-cyclodextrin are added to the beaker. Then 22.50 grams of Alcogum[®] L-511 are added to the beaker. 2.22 grams of lactic acid are then slowly added to the beaker dropwise. The mixture is then allowed to mix for an additional 10 minutes. The resulting composition will have a pH of about 4.

While particular embodiments of the present invention have been illustrated and described, it would be apparent to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

What is claimed is:

1. A malodor-controlling composition characterized in that it comprises:
 - (a) microcapsules containing at least one of the following:
 - (i) an active material; and
 - (ii) an optional encapsulated odor control agent;wherein said active material and said optional odor control agent may be contained in the same microcapsules; in different microcapsules; or both,
 - (b) an odor control agent outside of said microcapsules; and
 - (c) aqueous carrier.
2. The composition of Claim 1 wherein said microcapsules comprise a material selected from the group consisting of urea-formaldehydes, melamineformaldehydes, phenolformaldehydes, gelatin, poly(vinyl alcohol), poly(vinyl pyrrolidone), polyacrylates, polyamides, polyurethane, polymethacrylates, polyepoxides, cellulose acetate, cellulose nitrate, cellulose acetate butyrate, ethyl cellulose polyester, polychlorotrifluoroethylene, ethyl/vinyl acetate, saran, polystyrene, zein, paraffin wax, animal wax, vegetable wax, microcrystalline wax, polyethylene wax, poly(oxymethyleneurea), poly(oxymethylenemelamine), and mixtures thereof.
3. A composition according to any of the preceding claims wherein said microcapsules are present in said composition at a level of from 0.001% to 99.9% by weight of the composition, preferably at a level of from 0.001% to 1% by weight of the composition, and more preferably at a level of from 0.001% to 0.5% by weight of the composition.
4. A composition according to any of the preceding claims wherein said active material is selected from the group consisting of perfumes, flavoring agents, fungicide, brighteners, antistatic agents, wrinkle control agents, fabric softener actives, hard surface cleaning actives, skin and/or hair conditioning agents, antimicrobial actives, UV protection agents, insect repellants, animal/vermin repellants, flame retardants, and mixtures thereof.
5. A composition according to any of the preceding claims wherein said microcapsule has a particle size of from 0.001 micron to 1 millimeter, preferably from 1 micron to 500 microns, more preferably from 10 microns to 100 microns.

6. A composition according to any of the preceding claims wherein said odor control agents are selected from the group consisting of uncomplexed cyclodextrin, odor blockers, reactive aldehydes, flavanoids, zeolites, activated carbon, and mixtures thereof.
7. A composition according to any of the preceding claims wherein said odor control agent is present in said composition at a level of from 0.001% to 99.99% by weight of the composition, preferably at a level of from 0.001% to 20% by weight of the composition.
8. A composition according to any of the preceding claims wherein said aqueous carrier comprises water and is present in said composition at a level of at least 80% by weight of the composition.
9. A composition according to any of the preceding claims wherein said composition further comprises a dispersant, and said dispersant is preferably selected from the group consisting of pectine, alginate, arabinogalactan, carageenan, gellan gum, xanthum gum, guar gum, acrylates/acrylic polymers, water-swellable clays, fumed silicas, acrylate/aminoacrylate copolymers, and mixtures thereof.
10. A composition according to any of the preceding claims wherein said composition further comprises at least one of the following: free perfume that is not contained in said microcapsule, and a solvent.
11. A method of reducing or removing malodor from a surface having malodor, said method comprising the step of contacting said surface with a malodor-controlling composition according to Claim 1.

INTERNATIONAL SEARCH REPORT

Internat Application No
PCT/US 03/11530

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61L9/01 ✓ A61L9/012 ✓ A61L9/014 ✓ A61L9/14 ✓ A61L15/46 ✓
C11D3/50 / D06M13/00 / D06M23/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61L C11D D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 98 56340 A (PROCTER & GAMBLE) 17 December 1998 (1998-12-17) column 5, line 19 -column 7, line 12 column 14, line 3-13; claims 1,7; example V	1-11
Y	US 5 425 887 A (TSAUR LIANG S ET AL) 20 June 1995 (1995-06-20) column 2, line 13 -column 3, line 52 column 4, line 26 -column 5, line 23 column 7, line 5-27; claim 1	1-11
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- *&* document member of the same patent family

Date of the actual completion of the international search

17 June 2003

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 03/11530

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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